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CHEMICAL SCIENCES

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STUDIES ON THE FORMATION OF SODIUM CYANIDE FROM BARIUM CARBONATE AND SODIUM AZIDE¹

BY G. O. HENNEBERRY AND B. E. BAKER

Abstract

Attempts were made to prepare sodium cyanide by Adamson's method. Yields of only 36–37% were obtained and explosions occurred frequently during the initial heating operation. An apparatus was designed and a procedure developed whereby the rate of the initial reaction could be controlled. Conditions of reaction are described under which no explosions have been encountered. The effects of fusion temperature and length of fusion time were studied. Maximum yields of 79.4–84.9% were obtained by fusing at approximately 630°C. for 20 min.

Introduction

The reaction of radioactive barium carbonate – C^{14} with sodium azide to give labeled sodium cyanide was reported by Adamson (1) in 1947. His procedure consisted of heating sodium azide with barium carbonate in the ratio of 10 to 1 at the decomposition point of the azide, and finally fusing the mixture at a dull red heat for 10 min. The cyanide was recovered by adding dilute sulphuric acid and distilling into a slight excess of sodium hydroxide solution. The average yield was 78% and no mention was made of the occurrence of explosions.

Attempts to prepare sodium cyanide by this method, using nonradioactive materials, gave about half the yields reported by Adamson. Moreover, explosions occurred very frequently in the initial heating operation. The decomposition point of the barium carbonate – sodium azide mixture varied considerably, depending on the moisture content of the mixture, the crystal size of the azide, the degree of packing of the reactants, and the rate of heating.

Preliminary experiments showed that the occurrence of explosions could be reduced by thoroughly drying the azide and carbonate at 100°C. In many cases, however, a very fast reaction occurred without any warning, and, before the tube could be cooled sufficiently to decrease the rate of reaction, practically all the reactants had been carried from the tube by the escaping gases.

¹ Manuscript received in original form November 22, 1949, and, as revised, March 29, 1950. Contribution from the Chemistry Department and Tracer Laboratory, Faculty of Agriculture of McGill University, Macdonald College, Que.
Macdonald College Journal Series No. 260.

Attempts were made to reduce the rate of reaction by diluting the reactants with barium oxide. The rate of reaction, however, was not decreased appreciably by the addition of 1 to 4 gm. of the oxide to every gram of carbonate. Furthermore, no cyanide was recovered from any of the reaction mixtures.

During this investigation it was noted that if the reactants were heated extremely slowly a slight darkening occurred followed almost immediately by a violent reaction. In a few experiments the reaction mixture was cooled quickly enough to prevent the reaction from becoming violent. After the initial decomposition reaction was over, the tubes were fused at a dull red heat and the cyanide recovered as indicated in Adamson's procedure. Yields of 26-33%, calculated from barium carbonate, were obtained.

Apparently the reaction proceeded at a temperature somewhat lower than the temperature required for initiating the decomposition. This agreed with Moles' data (3) on the decomposition of azides at temperatures below the initial decomposition point. It seemed evident that if the reaction could be detected at an early stage and the temperature lowered slightly, the first step in the procedure could be carried out successfully.

It was noted that the temperature at which the reaction became explosive coincided fairly closely with the decomposition point of sodium azide. Tiede (4) reported that nitrogen was evolved in the thermal decomposition of alkali azides *in vacuo*. This suggested that the early stages of the reaction could be detected by measuring the increase in pressure due to the nitrogen formed during the decomposition.

Details of the apparatus and techniques used in studying the azide-carbonate reaction are given below.

Experimental

Materials

Sodium azide.—To a saturated solution of sodium azide (Sodium Trinitride Pure, Fisher Scientific Co.) at 40°C. was added two volumes of 95% alcohol. The precipitate which settled out on standing was redissolved in water and again precipitated by alcohol. This product was transferred to a Büchner funnel, washed with alcohol, then with ether, and dried on the funnel by suction. It was further dried at 100°C. in an oven for three hours. The caked mass was crushed with a spatula and stored in a tightly stoppered bottle away from light.

Barium carbonate.—The barium carbonate (Baker's Analyzed) was thoroughly ground in an agate mortar and dried to constant weight of 100°C.

Barium carbonate-sodium azide stock mixture.—Five grams of barium carbonate was finely ground and mixed thoroughly with 50 gm. of sodium azide. The mixture was stored in a desiccator away from light.

Decomposition Apparatus

The apparatus used for carrying out the reaction is shown in Fig. 1. The reaction tube *R* was a 15.0 by 1.6 cm. Pyrex test tube sealed to a 24/40 ground-glass joint. To the manifold *A* was attached a manometer *P* with a nearly horizontal arm to facilitate the detection of small changes in pressure. Flask *B* prevented large changes in pressure within the apparatus. Water was added to the reactants through *S*₁ after the fusion was carried out.

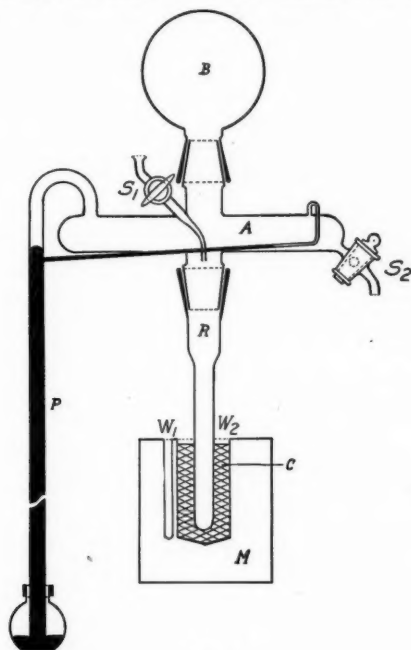


FIG 1.

M was a solid aluminum cylinder 10 cm. in diameter and 8 cm. high. Two holes, *W*₁ and *W*₂, were bored in one end to carry the reaction tube and thermocouple. This heating arrangement was similar to the one used by Dr. Bouthillier (2). Powdered carbon, *C*, which acted as a heat conductor between the tube and block, was placed in the central hole. Heat was applied to the aluminum block by means of a 500 w. Silex hot plate regulated with a Variac voltage control. Owing to the high thermal capacity of *M* it was possible to raise the temperature of the reaction tube very slowly, thus reducing the temperature gradient between the block and the contents of the tube to 0.5°C.

Distillation Apparatus.

Fig. 2 shows the apparatus used for recovering the cyanide from the azide-carbonate reaction mixture. The reaction tube *R* was fitted to the boiling

chamber *A* by means of a 24/40 ground-glass joint. *B* contained sulphuric acid which could be admitted to the reaction tube through stopcock *S*₁. The cap *D* was used so that a slight positive pressure could be applied to the acid to overcome the pressure of the air entrapped in *A*. Trap *T*₁ was constructed from a 1.5 cm. Pyrex tube and a coarse sintered glass plate *P* was sealed in at the bottom. It was attached to the water condenser *C* by means of rubber tubing. Standard sodium hydroxide solution was placed in *T*₁ and dilute silver nitrate solution in safety trap, *T*₂.

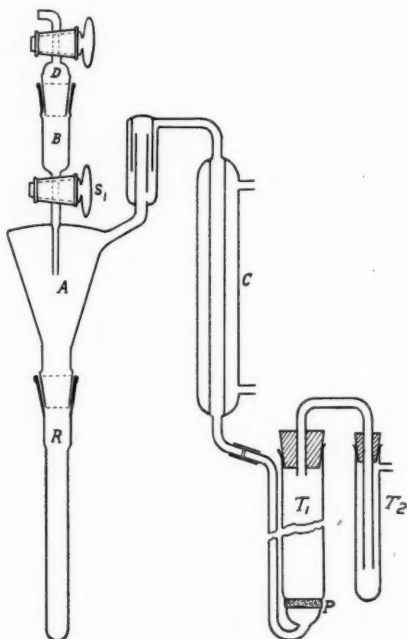


FIG. 2.

Procedure

One and one-tenth grams of the barium carbonate – sodium azide stock mixture was placed in the reaction tube. The ground-glass joint was sparingly greased, the tube joined to the manifold, and then the heating unit lifted into place. The temperature was quickly raised to 100°C. and the system evacuated through the stopcock *S*₂ by means of a Hyvac pump. Stopcock *S*₂ was then closed and the temperature slowly raised to the decomposition point of the azide. The manometer was watched carefully during this operation, and, as soon as a change in the level of the mercury in the horizontal arm was noted, the heating block was lowered until the end of the reaction tube was just below the surface of the carbon. The heater current was reduced slightly so that the temperature of the block slowly decreased five degrees. As the decomposition

proceeded the heating block was raised gradually until finally the reaction mixture was completely beneath the surface of the charcoal. The temperature was then raised 20° above the initial decomposition temperature and held there for a few minutes. As soon as the pressure within the system became constant, nitrogen was admitted through S_2 to balance atmospheric pressure and the aluminum block was replaced by a closely fitting muffle furnace. The desired temperature for fusing the reactants was attained in about two minutes.

After the heating period was over, the reaction tube was cooled to room temperature and 1 ml. of water added dropwise through S_1 , (Fig. 1). In this way any free sodium which was present was decomposed and the fused mass partially dissolved.

The reaction tube was then fitted to the distillation apparatus and 10 ml. of water was added through S_1 (Fig. 2), followed by 10 ml. of concentrated sulphuric acid. The reaction tube was heated with a Bunsen burner and 5 to 10 ml. of distillate collected in trap T_1 .

The percentage of sodium cyanide in the distillate was determined by titration with 0.0100 *N* silver nitrate in the presence of ammonia, using potassium iodide as indicator.

It was found necessary to use a new reaction tube for each experiment. At the high fusion temperature the reactants etched the walls of the tubes, which then activated the decomposition reaction in subsequent experiments. Using an etched tube, the temperature at which the decomposition commenced varied as much as 15° and the reaction was more difficult to control.

Results

I. Adamson's Method

A series of experiments was carried out using two stock mixtures of barium carbonate and sodium azide. One contained sodium azide (Eastman Kodak) dried at 105°C ., the other the recrystallized azide. The tendency for the decomposition reaction to become explosive was less with the stock mixture containing recrystallized azide. Of 30 runs made with the more stable mixture, 23 were discontinued owing to explosions and seven were carried through to completion. The average yield obtained in these experiments was approximately 30%.

II. Modified Method

Preliminary runs with the stock mixture of barium carbonate-sodium azide (recrystallized) showed that the decomposition was initiated at 347°C . In these experiments it was noted that the yield of cyanide depended on the temperature and length of fusion time. The aim of the experiments described below was to establish the optimum condition for fusion and the degree of reproducibility of results.

Effect of Fusion Temperature on Yield of Cyanide

Weighed amounts of the sodium azide-barium carbonate stock mixture (1.1 gm.) were decomposed in the vacuum apparatus, then fused at different temperatures for 20 min. The temperature range covered in these experiments was from 506°C. to 834°C. The yield of cyanide was found to increase with increased fusion temperatures and to reach a maximum between 600°C. and 700°C. At temperatures above 700°C. the odor of acetylene could be detected upon the addition of water to the fused mass, and in such samples a cloudy brownish solution was formed when the distillate was titrated with silver nitrate.

Effect of Duration of Fusion Period on Yield of Cyanide

A series of experiments was carried out at approximately 580°C. and 680°C. in which the fusion time was varied. The results of these experiments are shown in Table I. At the high temperature a five minute fusion period gave the greatest yield of cyanide. On longer periods of fusion, acetylene could be detected in the distillate which interfered with the cyanide determination. At the lower fusion temperatures maximum yields of cyanide were obtained after 20 min. heating. Somewhat smaller yields of cyanide were obtained with longer periods of heating, but no acetylene could be detected in the distillate of samples heated for less than 30 min.

TABLE I

YIELDS OF CYANIDE AT FUSION TEMPERATURES OF 680°C. AND 580°C.

Run No.	Fusion temperature, °C.	Heating time, min.	Titration, ml 0.01N AgNO ₃	Color of distillate after titration	Yield, %
1	681	5	10.6	Colorless	83.2
2	680	10	8.4	Light brown	—
3	686	15	4.6	" "	—
4	—	0	1.4	Colorless	11.0
5	583	5	3.8	"	29.9
6	585	10	4.8	"	37.8
7	580	15	6.3	"	49.2
8	586	18	8.4	"	66.3
9	579	20	9.6	"	75.3
10	584	22	8.5	"	67.2
11	590	25	8.1	"	63.8
12	580	30	5.4	Light brown	—

The above results indicated that the maximum yield of cyanide at 680°C. was somewhat greater than the maximum yield at 580°C. However, the five minute heating period was very critical and a slight variation greatly affected the yield of cyanide. A series of five experiments were carried out at approximately 630°C. with a 20 min. heating period. The yield of cyanide was $82 \pm 3\%$.

Acknowledgments

The authors wish to express their thanks to Dr. W. F. Oliver for his continued interest in this work and for many helpful suggestions.

Acknowledgment is made to the National Research Council of Canada for providing the funds which made this work possible.

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2. BOUTHILLIER, L. F. Private communication.
3. MOLES, E. *J. Chim. phys.* 16: 401. 1918.
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SYNTHESIS OF AMINO ACIDS FROM SUBSTITUTED CYANOACETIC ESTERS¹

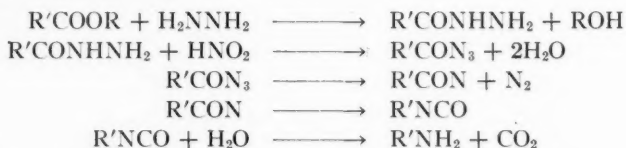
BY PAUL E. GAGNON, JEAN L. BOIVIN,²
AND JACQUES GIGUERE³

Abstract

The Darapsky method has been successfully applied to the synthesis of amino acids from substituted cyanoacetic esters, $RCH(CN)COOC_2H_5$. $R = CH_3CH(CH_2)_4CH_3$, $CH_3CH(CH_2)_5CH_3$, $CH_3(CH_2)_{11}$, $HOCH_2CH_2$, $o\text{-ClC}_6\text{H}_4CH_2$, $p\text{-CH}_3C_6H_4O(CH_2)_2$, $p\text{-CH}_3C_6H_4O(CH_2)_3$, $p\text{-C}_2H_5C_6H_4O(CH_2)_2$, $p\text{-C}_2H_5C_6H_4O(CH_2)_3$, $p\text{-ClC}_6H_4O(CH_2)_2$, $p\text{-ClC}_6H_4O(CH_2)_3$, $p\text{-BrC}_6H_4O(CH_2)_3$. The esters were prepared by condensation of cyanoacetic ester with suitable bromides. When treated with hydrazine hydrate, they gave rise to hydrazides, which were identified by their anisal derivatives. Azides were obtained by the action of nitrous acid on hydrazides at low temperature and were transformed by heating with alcohol into carbethoxyaminonitriles. Finally, the latter by hydrolysis yielded the following amino acids: *dl*- α -amino- β -methylcaprylic acid, *dl*- α -amino- β -methylpelargonic acid, *dl*- α -aminomyristic acid, *dl*- α -amino- γ -hydroxybutyric acid, *dl*- α -amino- γ -*p*-methylphenoxybutyric acid, *dl*- α -amino- δ -*p*-methylphenoxyvaleric acid, *dl*- α -amino- γ -*p*-ethylphenoxybutyric acid, *dl*- α -amino- δ -*p*-ethylphenoxyvaleric acid, *dl*- α -amino- γ -*p*-chlorophenoxybutyric acid, *dl*- α -amino- δ -*p*-chlorophenoxyvaleric acid, and *dl*- α -amino- δ -*p*-bromophenoxyvaleric acid.

Introduction

The Curtius reaction involves the preparation and degradation of an acyl azide usually prepared from an ester.



In 1915, Curtius applied this reaction to the synthesis of amino acids (3). It was the first attempt of this kind. As starting material, the potassium salt of monosubstituted malonic ester was used. The method was modified the same year by Darapsky and Hillers (5), who employed ethyl cyanoacetate as starting material instead of the monopotassium salt of malonic ester. The procedure gave excellent results for the synthesis of glycine. In 1936, Darapsky published a paper in which the synthesis of three other amino acids was described (4). Since then, more than 30 amino acids have been synthesized by the same methods (8, 9, 10, 11).

¹ Manuscript received February 22, 1950.

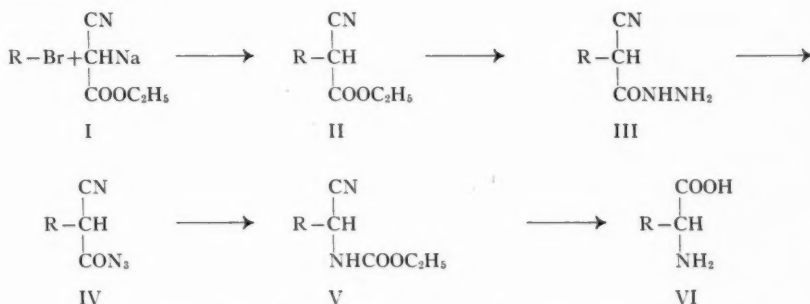
Contribution from the Department of Chemistry, Laval University, Quebec, Que. This paper constitutes a part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.

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³ Holder of a Price Bursary in 1948-1949. Holder of a Studentship under the National Research Council of Canada, 1949-1950.

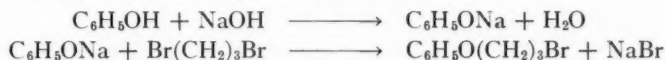
The present paper deals with the synthesis and description of 12 other amino acids.

The general procedure followed by Darapsky, which has been used for the preparation of the amino acids mentioned in this paper, is summarized as follows (I to VI).



R = *sec*-heptyl, $\text{CH}_3-\text{CH}-(\text{CH}_2)_4-\text{CH}_3$; *sec*-octyl, $\text{CH}_3-\text{CH}-(\text{CH}_2)_5-\text{CH}_3$; *n*-dodecyl, $\text{CH}_3(\text{CH}_2)_{11}$; β -hydroxyethyl, HOCH_2CH_2 ; *o*-chlorobenzyl, $\text{CH}_2-\text{C}_6\text{H}_4-\text{Cl}$; β -*p*-methylphenoxyethyl, $\text{p}-\text{CH}_3\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_2$; γ -*p*-methylphenoxypropyl, $\text{p}-\text{CH}_3\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_3$; β -*p*-ethylphenoxyethyl, $\text{p}-\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_2$; γ -*p*-ethylphenoxypropyl, $\text{p}-\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_3$; β -*p*-chlorophenoxyethyl, $\text{p}-\text{ClC}_6\text{H}_4\text{O}(\text{CH}_2)_2$; γ -*p*-chlorophenoxypropyl, $\text{p}-\text{ClC}_6\text{H}_4\text{O}(\text{CH}_2)_3$; γ -*p*-bromophenoxypropyl, $\text{p}-\text{BrC}_6\text{H}_4\text{O}(\text{CH}_2)_3$.

A few of the starting phenoxyalkyl bromides were prepared by a method that seems to be applicable to any phenol (2, 16).



The esters were made by condensing suitable halogenated radicals with the sodium derivative of cyanoacetic ester.

The formation of the hydrazides took place at room temperature when the esters were stirred with hydrazine hydrate. By treating the hydrazides with nitrous acid the corresponding azides were obtained. The urethanes were formed by heating the azides in alcoholic solution. Finally, the amino acids were obtained by heating the urethanes in hydrochloric acid (20%) for 48 hr. Longer periods of hydrolysis did not increase the yields.

When α -carbethoxyamino- γ -ethoxybutyronitrile was heated with hydrochloric acid (20%), the ethoxy group was transformed into a hydroxyl group and α -amino- γ -hydroxybutyric acid was formed instead of α -amino- γ -ethoxybutyric acid. Amino acids were prepared in a yield of 10 to 55% except in the case of α -aminomyristic acid, which was obtained in very small quantity.

Equal quantities by volume of water, concentrated hydrochloric acid, and formic acid (85%) were tried instead of hydrochloric acid (20%) to hydrolyze the urethanes but gave only traces of amino acids.

Experimental*

Substituted Phenoxypropyl Bromides (I)

The starting bromides were prepared in the following manner. In a three-liter round-bottomed flask, fitted with a stopper carrying a long reflux condenser, a mechanical stirrer, and a separatory funnel, were placed water (1 liter), trimethylene bromide (2.47 moles), and substituted phenol (1.95 moles). The stirrer was started and to the boiling solution was added a solution of sodium hydroxide (1.87 moles) in water (250 ml.) at such a rate that complete addition took about one hour. The mixture was refluxed for 10 to 15 hr., then cooled, and the upper water layer separated and discarded. The lower layer was washed with 5% sodium hydroxide to eliminate unreacted phenol and finally the mixture was washed with water. The solution was then distilled under reduced pressure.

In the case of the phenoxyethyl bromides, the quantities used in the preparations were different: 5.4 moles of ethylene bromide instead of 2.47 moles; 1.5 moles of phenol instead of 1.95 moles; 4.68 moles of sodium hydroxide instead of 1.87 moles.

The physical properties and yields of the bromides are summarized in Table I.

TABLE I
PHENOXYALKYL BROMIDES

Compound	B.p., ° C.	M.p., ° C.	Yield, %	Formula	Analysis, % hal.	
					Calc.	Found
β - <i>p</i> -Methylphenoxyethyl bromide*	130-138 (18 mm.)	40	56	$C_9H_{11}OBr$
γ - <i>p</i> -Methylphenoxypropyl bromide	155-160 (21 mm.)	..	66	$C_{10}H_{13}OBr$	34.8	35.0
β - <i>p</i> -Ethylphenoxyethyl bromide	156-160 (20 mm.)	..	58	$C_{10}H_{13}OBr$	34.8	34.4
γ - <i>p</i> -Ethylphenoxypropyl bromide	173-178 (24 mm.)	..	70	$C_{11}H_{15}OBr$	32.8	32.3
β - <i>p</i> -Chlorophenoxyethyl bromide	155-163 (18 mm.)	41-42	50	C_8H_9OBrCl	48.9	48.1
γ - <i>p</i> -Chlorophenoxypropyl bromide	178-181 (24 mm.)	..	66	$C_9H_{10}OBrCl$	46.2	45.5
γ - <i>p</i> -Bromophenoxypropyl bromide†	180-190 (18 mm.)	49.5	65	$C_9H_{10}OBr_2$

*Previously prepared by Schreiber (17).

†Previously prepared by Jones (15).

Substituted Cyanoacetic Esters (II)

To a solution of sodium (11.5 gm., 0.5 mole) in absolute ethyl alcohol (200 ml.) was added ethyl cyanoacetate (113 gm., 1.0 mole), and, after cooling, the suitable bromide or chloride (0.5 mole). The mixture was refluxed on a water bath until neutral to wet litmus paper. Then the alcohol was evaporated and the oily layer was poured into cold water (about 750 ml.). After acidification with hydrochloric acid, the mixture was extracted two or three times with ether. The dry ethereal solution was evaporated and the residue fractionated under reduced pressure.

*All melting points are uncorrected.

The yields and properties of monosubstituted cyanoacetic esters are given in Table II.

TABLE II

ETHYL α -SUBSTITUTED CYANOACETATES, $RCH(CN)COOC_2H_5$

R	Starting material	Yield %	B.p., ° C.	Formula	Nitrogen, %		n_D^{20}
					Cal.	Found	
sec-Heptyl	$CH_3-CH-(CH_2)_4-CH_3$	71	153-158 (17 mm.)	$C_{12}H_{21}O_2N$	6.63	6.50	1.4360 ²⁴
sec-Octyl*	$CH_3-\overset{Br}{\underset{ }{CH}}-(CH_2)_5-CH_3$	63	154-162 (13 mm.)	$C_{13}H_{23}O_2N$	6.22	6.30	1.4359 ²⁵
n-Dodecyl	$CH_3-(CH_2)_{11}Br$	75	194-204 (13 mm.)	$C_{17}H_{33}O_2N$	5.00	5.10	1.4465 ²⁴
β -Ethoxyethyl	$C_2H_5O(CH_2)_2Br$	65	128-135 (15 mm.)	$C_9H_{19}O_3N$	7.56	7.44	1.4282 ²³
o-Chlorobenzyl	$o-ClC_6H_4CH_2Cl$	42	196-204 (20 mm.)	$C_{12}H_{11}O_2ClN$	5.90	6.01	1.5162 ²⁵
β -p-Methylphenoxyethyl	$p-CH_3C_6H_4O(CH_2)_2Br$	62	202-210 (13 mm.)	$C_{14}H_{17}O_2N$	5.66	5.45	1.5052 ²⁴
γ -p-Methylphenoxypropyl	$p-CH_3C_6H_4O(CH_2)_3Br$	74	210-215 (13 mm.)	$C_{15}H_{19}O_2N$	5.36	5.23	1.5035 ²⁴
β -p-Ethylphenoxyethyl	$p-C_2H_5C_6H_4O(CH_2)_2Br$	60	200-210 (13 mm.)	$C_{13}H_{19}O_2N$	5.36	5.37	...
γ -p-Ethylphenoxypropyl	$p-C_2H_5C_6H_4O(CH_2)_3Br$	70	212-218 (13 mm.)	$C_{14}H_{21}O_2N$	5.09	5.20	1.5019 ²⁷
β -p-Chlorophenoxyethyl	$p-ClC_6H_4O(CH_2)_2Br$	52	212-218 (14 mm.)	$C_{12}H_{11}O_2ClN$	5.23	5.18	1.5220 ²³
γ -p-Chlorophenoxypropyl	$p-ClC_6H_4O(CH_2)_3Br$	66	216-226 (14 mm.)	$C_{13}H_{13}O_2ClN$	5.00	4.92	1.5143 ²⁴
γ -p-Bromophenoxypropyl	$p-BrC_6H_4O(CH_2)_3Br$	65	230-238 (12 mm.)	$C_{14}H_{15}O_2BrN$	4.29	4.35	1.5276 ²⁴

*Previously prepared by Alexander and Cope (1).

†Viscous liquid.

Substituted Cyanoacethydrazides (III)

The esters (0.1 mole) were stirred vigorously for a few minutes with hydrazine hydrate (100%, 0.1 mole). There was evolution of heat, and most of the hydrazides solidified readily. They were recrystallized from dilute ethanol. The properties are listed in Table III.

TABLE III

 α -SUBSTITUTED CYANOACETHYDRAZIDES ($RCH(CN)CONHNH_2$)

R	M.p., ° C.	Formula	Nitrogen, %	
			Calc.	Found
sec-Heptyl*	$C_{10}H_{19}O_2N_3$
sec-Octyl*	$C_{11}H_{21}O_2N_3$
n-Dodecyl	92 - 94	$C_{13}H_{25}ON_3$	15.7	15.5
β -Ethoxyethyl*	$C_7H_{13}O_2N_3$
o-Chlorobenzyl	113 - 114	$C_{10}H_9OCIN_3$	18.8	18.7
β -p-Methylphenoxyethyl	111 - 112	$C_{12}H_{15}O_2N_3$	18.0	18.0
γ -p-Methylphenoxypropyl	87 - 88	$C_{13}H_{17}O_2N_3$	17.0	17.0
β -p-Ethylphenoxyethyl	104 - 106	$C_{13}H_{17}O_2N_3$	17.0	17.2
γ -p-Ethylphenoxypropyl	94 - 95	$C_{14}H_{19}O_2N_3$	16.1	16.0
β -p-Chlorophenoxyethyl	111 - 112	$C_{11}H_{12}O_2ClN_3$	16.5	16.2
γ -p-Chlorophenoxypropyl	100 - 101	$C_{12}H_{14}O_2ClN_3$	15.7	15.8
γ -p-Bromophenoxypropyl	132 - 133	$C_{12}H_{14}O_2BrN_3$	13.4	13.2

*These hydrazides were viscous liquids and have been identified by means of their anisal derivatives.

Anisal Derivatives of Substituted Cyanoacethydrazides

The cyanoacethydrazides dissolved in alcohol were stirred with anisaldehyde and cooled. White crystals separated out. These were purified by repeated crystallization from ethanol. In the case of the liquid cyanoacethydrazides many crystallizations were necessary before the desired derivatives could be obtained pure.

The physical constants are summarized in Table IV.

TABLE IV
ANISAL DERIVATIVES $RCH(CN)CONHN = CHC_6H_4OCH_3$

R	M.p., ° C.	Formula	Nitrogen, %	
			Calc.	Found
<i>sec</i> -Heptyl	111 - 112	$C_{15}H_{23}O_2N_3$	13.3	13.5
<i>sec</i> -Octyl	108	$C_{16}H_{25}O_2N_3$	12.8	13.1
<i>n</i> -Dodecyl	110 - 111	$C_{22}H_{35}O_2N_3$	10.9	11.1
β -Ethoxyethyl	110 - 111	$C_{15}H_{19}O_3N_3$	14.5	14.2
<i>o</i> -Chlorobenzyl	168 - 169	$C_{15}H_{13}O_2ClN_3$	12.3	12.2
β - <i>p</i> -Methylphenoxyethyl	169	$C_{20}H_{21}O_2N_3$	11.9	11.9
γ - <i>p</i> -Methylphenoxypropyl	157 - 158	$C_{21}H_{23}O_2N_3$	11.5	11.2
β - <i>p</i> -Ethylphenoxyethyl	166 - 167	$C_{21}H_{23}O_2N_3$	11.5	11.4
γ - <i>p</i> -Ethylphenoxypropyl	128 - 129	$C_{22}H_{25}O_2N_3$	11.0	10.8
β - <i>p</i> -Chlorophenoxyethyl	143 - 144	$C_{19}H_{15}O_2ClN_3$	11.3	11.4
γ - <i>p</i> -Chlorophenoxypropyl	174 - 175	$C_{20}H_{17}O_2ClN_3$	10.8	10.5
γ - <i>p</i> -Bromophenoxypropyl	172 - 173	$C_{20}H_{17}O_2BrN_3$	9.7	9.7

Amino Acids (VI)

The hydrazides (0.1 mole) in suspension or dissolved in hydrochloric acid (15%, 200 ml.) were mixed with ether (100 ml.) and treated at 0° C. with a solution of sodium nitrite (10 gm.) in water (25 ml.). The azides passed into the ether layer as soon as they were formed. Then the ethereal solutions of azides were decanted and the aqueous layer was extracted rapidly twice with ether. The combined ethereal solutions were dried over anhydrous sodium sulphate. To this solution absolute ethyl alcohol (100 ml.) was added. The ether was distilled off, leaving the alcohol. The alcoholic solution was refluxed for about one hour to complete the formation of the urethane. The latter was hydrolyzed in an aqueous solution of hydrochloric acid (20%) for 48 hr.

The solution was evaporated many times to dryness to remove all the hydrochloric acid, the residue being dissolved in hot water after every evaporation. The final residue was dissolved in water. The solution was treated with activated charcoal, filtered, evaporated to a small volume, and its pH adjusted to 6 with ammonia.

dl- α -Amino- γ -hydroxybutyric acid, *dl*- α -amino- β -methylcaprylic acid, *dl*- α -amino- β -methylpelargonic acid, *dl*-*o*-chlorophenylalanine, and *dl*- α -amino- γ -*p*-chlorophenoxybutyric acid were isolated by the lead oxide method (12).

The properties and physical constants are shown in Table V.

TABLE V
AMINO ACIDS AND DERIVATIVES

Amino acids		Derivatives of amino acids				
Compound	Yield, %	Compound	M.p., °C.	Formula	Nitrogen, %	
					Calc.	Found
<i>dl</i> - α -Amino- β -methylcaprylic acid	20	Phenylureido	157 - 159	C ₁₆ H ₂₀ O ₃ N ₂	9.58	9.78
<i>dl</i> - α -Amino- β -methylpelargonic acid	17	Phenylureido	154 - 156	C ₁₇ H ₂₀ O ₃ N ₂	9.28	9.40
<i>dl</i> - α -Amino- γ -hydroxybutyric acid*	55	Copper Derivative	238 - 240	C ₁₅ H ₁₈ O ₅ CuN ₂	9.35	9.13
<i>dl</i> - α -Chlorophenylalanine**	42	Hydantoin	174 - 175	C ₁₀ H ₉ O ₂ ClN ₂	12.4	12.5
<i>dl</i> - α -Amino- γ - <i>p</i> -methylphenoxybutyric acid	28	Hydantoin	174 - 175	C ₁₂ H ₁₅ O ₃ N ₂	11.9	11.7
<i>dl</i> - α -Amino- δ - <i>p</i> -methylphenoxyvaleric acid	21	Hydantoin	157 - 158	C ₁₂ H ₁₆ O ₃ N ₂	11.3	11.3
<i>dl</i> - α -Amino- γ - <i>p</i> -ethylphenoxybutyric acid	14	Hydantoin	174 - 175	C ₁₂ H ₁₆ O ₃ N ₂	11.3	11.5
<i>dl</i> - α -Amino- δ - <i>p</i> -ethylphenoxyvaleric acid	10	Phenylureido	152 - 153	C ₂₀ H ₂₄ O ₄ N ₂	7.86	8.02
<i>dl</i> - α -Amino- γ - <i>p</i> -chlorophenoxybutyric acid	15	Hydantoin	176 - 178	C ₁₁ H ₁₁ O ₃ ClN ₂	11.0	11.1
<i>dl</i> - α -Amino- δ - <i>p</i> -chlorophenoxyvaleric acid	13	Phenylureido	172 - 173	C ₁₈ H ₁₉ O ₄ ClN ₂	7.72	7.73
<i>dl</i> - α -Amino- δ - <i>p</i> -bromophenoxyvaleric acid	18	Phenylureido	183 - 184	C ₁₈ H ₁₉ O ₄ BrN ₂	6.92	6.90

Only traces of *dl*- α -aminomyristic acid were obtained (13).

*Ref. (6, 7).

**Ref. (14).

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THE KINETICS OF CUPRENE GROWTH¹BY ADRIEN E. LÈGER² AND CYRIAS OUELLET

Abstract

The kinetics of the polymerization of acetylene to cuprene on a copper catalyst between 200° and 300° C. have been studied manometrically in a static system. The maximum velocity of the autocatalytic reaction shows a first-order dependence upon acetylene pressure. The reaction is retarded in the presence of small amounts of oxygen but accelerated by preoxidation of the catalyst. The apparent activation energy, of about 10 kcal. per mole for cuprene growth between 210° and 280° C., changes to about 40 kcal. per mole above 280° C. at which temperature a second reaction seems to set in. Hydrogen, carbon monoxide, or nitric oxide has no effect on the reaction velocity. Series of five successive seedings have been obtained with cuprene originally grown on cuprite, and show an effect of aging of the cuprene.

Introduction

In view of the renewed interest in the growth and properties of insoluble addition polymers, it is desirable to obtain new information on the reaction in which the simple molecule acetylene, in the presence of copper or its oxides, forms the light, fibrous, and insoluble solid known as cuprene.

First prepared by Erdmann and Koethner (8) and later named by Sabatier and Senderens (20), cuprene has been assigned a variety of formulas (8, 14, 20) showing more or less important deviations from the composition $(C_2H_2)_n$ accepted by Calhoun (4). Kaufmann and Monhaupt (13) showed that it is inert towards all ordinary chemicals, reacts difficultly with halogens, and is oxidized by nitric acid to mellitic acid. Its insolubility and its tendency not to swell in any known solvent characterize it as a three-dimensional polymer (4). Its texture and color vary with the reaction temperature and with the catalyst used in its preparation (5, 7, 10, 20). The fibrous structure of cuprene differs from the structure of polymers formed by the action of radiations upon acetylene gas, as shown by the electron microscopic studies of Watson and others (22). Additional information on cuprene can be found in the monographs of Nieuwland (16) and Piganiol (19) on acetylene.

In discussing the mechanism of the reaction, Sabatier and Senderens (20) suggested the formation of unstable copper acetylide as the primary step. Bates and Taylor (2) proposed a chain mechanism. In what seems to be the only kinetic study of this polymerization, Calhoun (4) followed the reaction catalyzed by cupric oxide under constant acetylene pressure in a flow system. He observed an induction period, gave an equation which describes the course of the reaction, discussed the possible roles of surface and diffusion effects in

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this heterogeneous reaction, and estimated the heat of the polymerization as 70 kcal. per mole. Akopyan and Gyuli-Kevkyan (1) studied the production of cuprene from monovinylacetylene as well as from acetylene. From their results, they conclude that monovinylacetylene is probably not an intermediate product of the reaction.

The kinetic study of insoluble polymer has been initiated recently by the work of Kharasch (15), Welch (24), Winkler (6, 12), and their coworkers on butadiene and butadiene-styrene "popcorn" polymers. In the light of their findings, it appeared desirable to conduct a parallel investigation of the formation of cuprene, in which reaction the phenomena of surface catalysis and growth of a solid phase are intimately connected. The kinetic aspects of this work of an exploratory nature are described in the present paper; the results of an electron microscopic examination of the cuprene samples, carried out by Dr. J. H. L. Watson, will be published elsewhere (23).

Experimental

The polymerization of gaseous acetylene took place in a static system on a suitable catalyst, generally copper wire. The reaction was followed at constant volume by measuring manometrically the decreasing pressure. The reaction vessel, a 180 cm.³ Pyrex tube, was enclosed in a tubular, horizontal iron furnace in which the temperature was kept constant and uniform within $\pm 0.5^\circ\text{C}$. The vessel was evacuated through a dry-ice trap by means of a mechanical pump or diffusion pump filled with D.C. 703 silicone oil. The total volume, including the trap, manometer and large-bore connections, was 300 cm.³. By means of a 5 cm.³ measuring tube, connected to the system by a three-way stopcock, known quantities of foreign gases could be introduced before or during the reaction. The manometers were mercury-filled and "Apiezon M" was used as a lubricant for ground joints and stopcocks. In actual operation, the reaction vessel containing the catalyst was evacuated at the temperature of the reaction for about 30 min. and the acetylene was then introduced rapidly.

For qualitative observations and for the growth of samples used in the seeding experiments, a multiple reaction vessel was used which consisted of five parallel Pyrex tubes 1 by 10 cm., placed horizontally in a furnace in which the temperature was constant within about 5°C .

The acetylene used was "Prest-O-Lite" (welding grade) and was obtained in cylinders. It was first washed through six towers which contained respectively (1) 40% sodium bisulphite to absorb acetone, (2) chromic acid, (3) 50% mercuric chloride in concentrated hydrochloric acid to remove phosphine, arsine, hydrogen sulphide, ammonia, and silane, (4) 36% potassium hydroxide to remove gaseous hydrochloric acid, (5) alkaline sodium hydro-sulphite to absorb oxygen, and (6) 36% potassium hydroxide to remove sulphur dioxide. The sequence of scrubbing towers was essentially that proposed by

Farkas and Melville (9). The acetylene was then stored over phosphorus pentoxide. It was purified before use by fractional distillation from a liquid-air trap.

The oxygen and electrolytic hydrogen were taken from commercial cylinders; the nitric oxide from a "Matheson" lecture bottle 99% NO. The carbon monoxide was prepared from formic and sulphuric acids and passed over soda lime. All these gases were stored over phosphorus pentoxide.

Copper wire was used as a catalyst in all the quantitative experiments. This catalyst was prepared by winding 2.5 m. of wire into a coil about 1 cm. in diameter. The coil was washed with toluene or ether, dried in the air, and introduced immediately into the reaction vessel. This provided a standard catalyst of high purity with a uniform surface but flexible structure and minimized the diffusion effects associated with the use of powders. All the catalysts were taken from the same spool of No 18, Brown and Sharp, "medium hard drawn" copper wire of 1.024 mm. diameter at 20° C. Two meters of this wire had an apparent area of 62.7 cm.²

Results

A. QUALITATIVE OBSERVATIONS

Reactions with Various Catalysts

A series of qualitative trials was made in order to choose the most suitable catalyst and experimental conditions. Most of these experiments were carried out at initial acetylene pressures of between 20 and 30 cm. of mercury and at 275° C. A "normal" reaction is one in which half the acetylene was taken up in a period of time of the order of one hour.

No reaction was observed with the following catalysts: copper turnings washed in nitric acid and distilled water, brass turnings (unoxidized) before introduction of about 2% air, crystals of octahedral pyrite, cobaltine, hematite, magnetite, galena, powders of ferric oxide, cadmium, stannic and nickel oxides and Pyrex glass. Slow reactions were obtained with powdered cuprous oxide, cupric oxide in wire form, some copper wires and copper foil previously reduced in hydrogen at 440° C. There were slow reactions with formation of liquid products on cupric oxide powder and on copper wire in the presence of 1.7% air. "Normal" reactions were obtained with copper turnings oxidized in air by heating to dull red and with copper wire in the absence or presence of 1.5% air in the reaction vessel.

Cuprite crystals, detached from a sample of the mineral, differed from powdered cuprous oxide in that the former gave very rapid reactions even at 220° C., while the latter did not. These reactions were studied by observing the growth by means of a binocular microscope with a magnification of 54 diameters. The growth took place in a small tubular reaction chamber, the heating of which could be interrupted at will. The reaction was very slow in

getting under way, nothing being visible for several minutes. Then, red spots distributed at random appeared on the various crystal faces. Once these initiation centers had been formed, cuprene growth was very rapid. In a few minutes, the crystal was completely covered with the polymer, which soon grew into a sponge-like mass in which it was difficult to see filaments at the magnification used.

Seeding of Cuprene

Cuprene can act as its own catalyst as was noticed by Sabatier and Senderens (20). A small particle of cuprene from cuprite-catalyzed growth was detached from a point in the spongy lump several millimeters from the embedded cuprite crystal and used as a seed for a second polymerization. From this new growth obtained, a particle was again detached and used as a seed for a third growth, and so on. Two series of five successive polymerizations were thus studied. In each series, the reactivity decreased markedly after each new seeding and the color changed from a dark brown for the original cuprene to a light orange-yellow for the last growth. There was also an evolution in the apparent texture of the cuprene; the underlying structural changes, as revealed in electron-microscopic observations by Dr. J. H. L. Watson, will be described elsewhere (23). In one of these experiments a little oxygen leaked into the reaction chamber, causing carbonization of the cuprene and rendering it inactive as a catalyst.

It was observed that the cuprene, a light and fluffy mass, carried a positive electric charge which it could retain for several days, and which probably resulted from the electrostatic effects of flowing gases or from triboelectric charging during growth.

B. KINETIC MEASUREMENTS

General Features

Typical reaction curves are shown in Fig. 1 and the conditions under which they were obtained are listed in Table I. Duplication of several experiments showed that these curves were reproducible with an accuracy of about 5%. Most of the curves exhibit a brief induction period, followed by a phase during which the pressure decrease is approximately linear with time. This is followed by a gradual slowing down of the reaction which, however, may proceed for periods of 5 to 10 hr. before the pressure attains a constant value. These slow changes are not shown on the figures, but the final pressures are given in the tables. The small quantity of residual gases, products of unknown side reactions, shows no clear correlation with the experimental conditions. Its incomplete condensation at liquid air temperature shows that it is a mixture. According to Calhoun (4), it consists mainly of ethylene, ethane, and hydrogen.

Various assumptions regarding the rates of initiation and growth of cuprene fibers failed to yield a kinetic expression capable of fitting more than a few of our results. Therefore, for purposes of comparison the maximum slope of

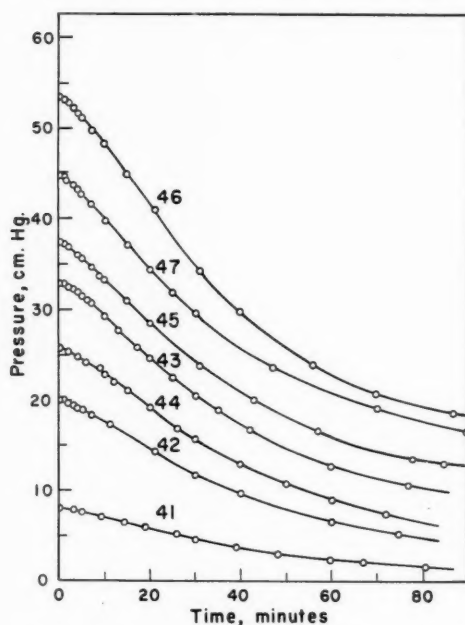


FIG. 1. Pressure as a function of time during reactions at 250° C. and various initial acetylene pressures.

TABLE I
EFFECT OF PRESSURE ON REACTION RATE
Catalyst: 2.5 m. of copper wire
Temperature: 250° C.

Reaction No.	Pressure, cm. Hg		Induction period, min.	$k \times 10$ 0° C.
	Initial	Final		
41	8.0	0.6	5	0.68
42	20.0	1.0	5	1.53
44	25.7	1.6	3	1.87
43	32.8	2.4	2	2.31
45	37.4	4.5	2	2.46
47	44.8	—	2	2.92
46	53.3	9.0	2	3.60

each curve, coinciding with its linear portion, has been taken as the measure of the reaction velocity. In order to compare rates of acetylene consumption, the pressure decreases have been converted to 0° C., using the ideal gas law. Each reaction is characterized by a value of the reaction rate

$$k = - \left(\frac{\Delta P}{\Delta t} \right)_{0^\circ \text{C.}}$$

where P is expressed in centimeters of mercury and t in minutes.

A series of reactions was carried out at 250° C., the only variable being the initial acetylene pressure. The results obtained are given in Table I; the various reaction curves are shown graphically in Fig. 1. In Fig. 2, the value of k is given as a function of the initial pressure of acetylene. The reaction rate k is almost directly proportional to the initial acetylene pressure.

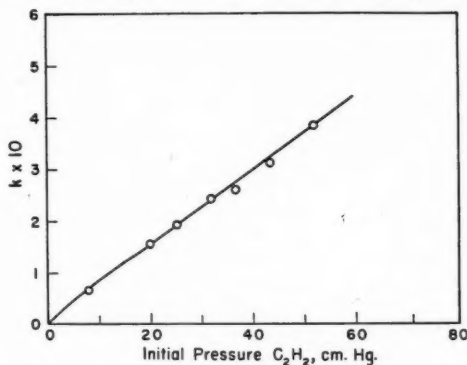


FIG. 2. Reaction velocity as a function of initial acetylene pressure. The values of k are given in Table I. Temperature of reactions, 250° C.

The activity of the cuprene (or of the catalyst) decreases as the reaction proceeds. This aging effect is shown by the fact, illustrated in Fig. 3, that introducing fresh acetylene does not restore the initial velocity.

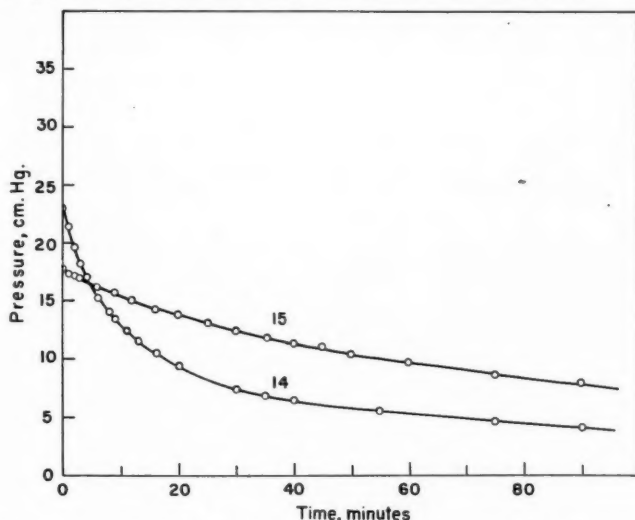


FIG. 3. Two consecutive reactions with the same catalyst. At the end of Reaction 14, the residual gases were pumped out and pure acetylene introduced into the reaction vessel to obtain Reaction 15. The catalyst was 1 m. of copper wire, and the reaction temperature, 275° C.

Effect of Oxygen

In view of the well known ability of unstable peroxides to initiate certain polymerization processes and also of the fact that cuprene can grow on either copper or one of its oxides, it was interesting to investigate the effect of small quantities of oxygen under various conditions. Fig. 4 shows the acceleration obtained by preheating the copper wire in 76 cm. of oxygen at 300° C. and 440° C. The effect is considerable and does not seem to be increased by prolonging the treatment or using temperatures above 300° C. When reactions were carried out on a normal copper catalyst with acetylene containing a small quantity of oxygen, both the induction period and the maximum re-

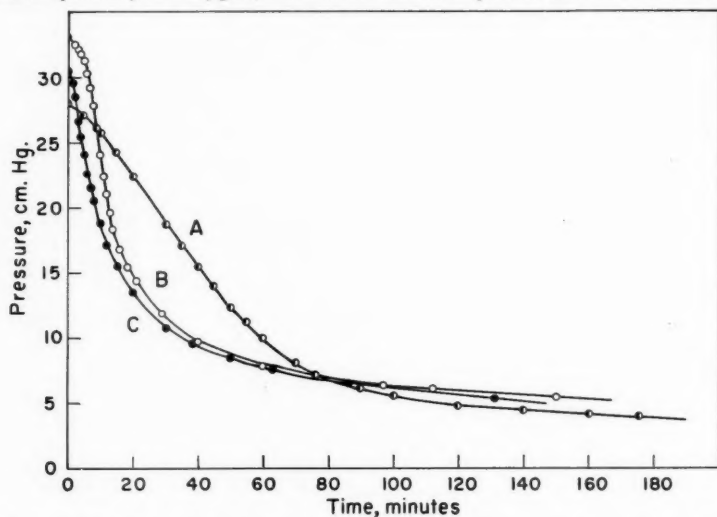


FIG. 4. Effect of surface oxidation of the catalyst. Curve A, with a nonoxidized catalyst; Curve B, catalyst oxidized one hour at 440° C. and Curve C, catalyst oxidized five minutes at 300° C., both under 76 cm. pressure of oxygen. The catalyst was 2.5 m. of copper wire; reaction temperature, 256° C.

TABLE II
EFFECT OF OXYGEN ON INDUCTION PERIOD AND VELOCITY CONSTANT k .
REACTIONS AT 250° C. ON 2.5 m. COPPER WIRE

Run No.	Pressure, cm. Hg			Induction period, min.	$k \times 10$ at 0° C.
	O ₂	C ₂ H ₂	Final		
<i>Oxygen introduced after acetylene</i>					
44	0.0	25.7	1.6	3	1.87
63	0.2	26.9	...	5	1.79
76	0.6	27.3	1.6	7	1.80
74	1.2	26.9	2.9	11	1.74
75	1.9	27.3	...	15	1.49
<i>Oxygen introduced before acetylene</i>					
44	0.0	25.7	1.6	3	1.87
77	0.4	27.3	1.2	10	1.44
79	0.8	26.5	2.7	20	1.44
78	1.3	27.1	2.2	42	1.54

action velocity were affected, as shown in Table II and Figs. 5 and 6. In one series of experiments, the oxygen was introduced immediately (within five seconds) after the acetylene. There was a slight decrease in the maximum reaction velocity and considerable lengthening of the induction period. Introducing the oxygen immediately before the acetylene also lengthened the induction period and lowered the maximum velocity more markedly. Both effects were the opposite of that caused by preoxidation of the catalyst. The arbitrary values of the induction periods given in Table II were obtained by extrapolating the linear portions of the curves backwards to the points where they cut the horizontal lines corresponding to the initial pressures. Further oxygen effects will be considered below, in connection with the temperature coefficient.

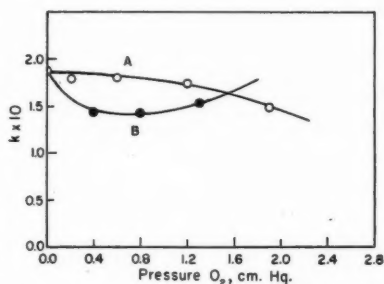


FIG. 5. Influence of the addition of oxygen on reaction velocity. Curve A gives k as a function of initial oxygen pressure when it is introduced into the reaction chamber a few seconds after the acetylene. Curve B, gives k , also as a function of initial oxygen pressure, but when it is introduced into the reaction chamber before the acetylene. Temperature of the reaction, 250°C .

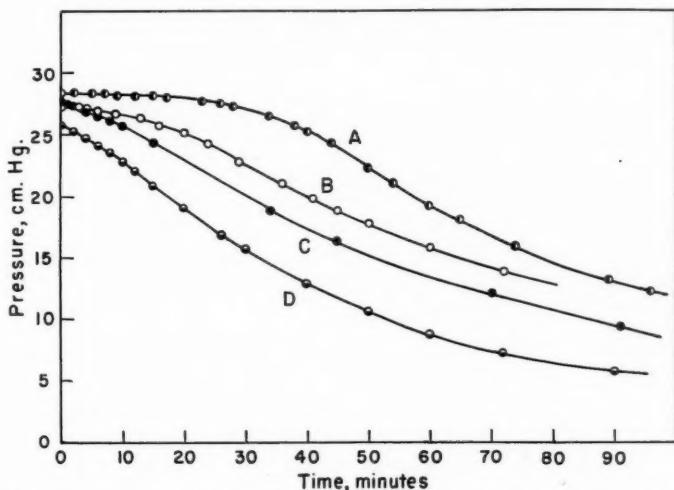


FIG. 6. Influence of oxygen on the length of the induction period. Oxygen was introduced into the reaction chamber a few seconds before the acetylene. Curve A refers to Reaction 78, B to Reaction 79, C to Reaction 77, and D to Reaction 44 in Table II.

Addition of Hydrogen, Carbon Monoxide, and Nitric Oxide

The results obtained with oxygen suggested the use of a reducing gas, although it appeared doubtful if that would introduce any appreciable difference in view of the reducing power of acetylene itself. In fact, neither the induction period nor the maximum velocity was changed when the catalyst was preheated for three hours in hydrogen at 76 cm. or when small quantities of hydrogen were mixed with the acetylene. Preheating the catalyst for one hour at 250° C. in 31.8 cm. of carbon monoxide or mixing small quantities of this gas with the acetylene also had practically no effect. This suggests that the catalytic action of the copper in this reaction does not involve the same active spots which operate in the catalytic reductions poisoned by carbon monoxide.

In the hope of finding whether free radicals play a part in the initiation or growth of cuprene, reactions were carried out with acetylene to which 1.9% nitric oxide (NO) was added immediately upon the introduction of the acetylene into the reaction vessel. The maximum reaction velocity was not affected, but there was a very slight increase in the induction period which could be attributed to other causes. At any rate, these negative results are inconclusive, since nitric oxide is known to react with acetylene (11) and may have been removed in the early stages of the reaction.

Temperature Effect

In preliminary qualitative runs, it was found that the effect produced by an elevation in temperature was very great at high temperatures, much less at lower temperatures, and that the reaction velocity seemed to pass through a maximum at some intermediate point. In order to verify this and to evaluate this effect more precisely a series of reactions at different temperatures was carried out. The catalyst used in all these was 2.5 m. of copper wire washed in ether. A few representative reaction curves are given in Fig. 7 and the experimental results, in Table III.

The reaction velocity increased gradually from 210° to 275° C., became irregular at this temperature, and increased more rapidly from 280° to 320° C. At temperatures beyond 280° C., the induction period had disappeared and there seemed to be more liquid hydrocarbons formed, while the cuprene was darker and of smaller volume.

Following a series of experiments with pure acetylene, it was thought possible that a mixture of acetylene and oxygen would show a similar maximum. Several reactions were carried out with a mixture of about 27 cm. acetylene and 0.2 cm. oxygen at various temperatures. The oxygen was introduced into the reaction vessel a few seconds after the acetylene, so as not to oxidize the catalyst. The results are given in Table IV, and a few representative curves are shown in Fig. 8.

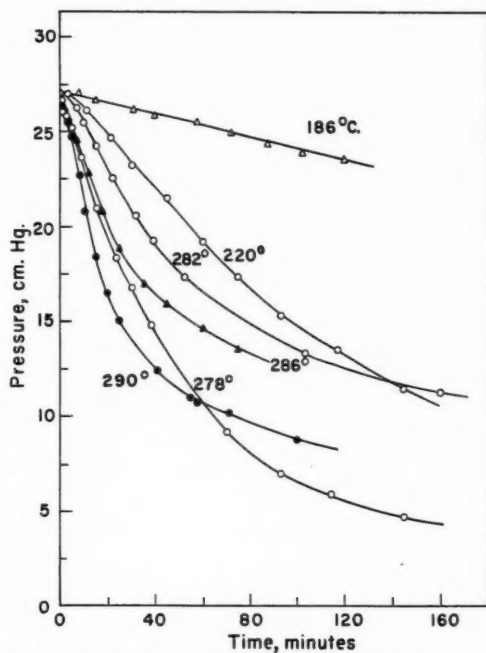


FIG. 7. Pressure as a function of time for reactions at different temperatures for pure acetylene

TABLE III
THE EFFECT OF TEMPERATURE ON REACTION RATE
Reactions without oxygen.
Catalyst: 2.5 m. of copper wire

Reaction No.	Temp., °C.	$1/T \times 10^4$, °K.	Pressure, cm.Hg		$k \times 10$ 0° C.
			Initial	Final	
60	186	21.79	27.4	4.7	0.20
37	210	20.70	32.2	1.8	0.78
57	220	20.28	27.3	3.7	0.88
39	230	19.88	27.1	1.4	1.11
58	244	19.34	27.3	3.7	1.29
44	250	19.12	25.7	1.6	1.87
30	256	18.90	28.0	2.2	1.87
32	274	18.28	26.8	—	1.66
52	276	18.18	27.5	3.9	2.39
51	278	18.15	27.7	3.9	1.48
50	278	18.15	27.1	—	3.17
53	280	18.08	27.1	3.7	3.09
55	280	18.08	27.1	3.5	2.12
49	282	18.02	27.3	3.3	1.12
54	286	17.89	26.7	3.7	1.83
34	290	17.76	27.0	1.6	1.78
62	296	17.57	27.6	2.7	2.98
56	302	17.39	26.9	2.9	4.18
40	320	16.86	27.1	3.1	8.65

TABLE IV

EFFECT OF TEMPERATURE ON REACTION RATE
REACTIONS IN THE PRESENCE OF 0.2 CM. OF OXYGEN

Catalyst: 2.5 m. of copper wire

Reaction No.	Temp., °C.	$1/T \times 10^4$, °K.	Pressure, cm.Hg		$k \times 10$ °C.
			Initial	Final	
66	226	20.04	27.5	1.8	1.07
70	238	19.57	27.5	1.4	1.41
63	250	19.12	27.1	—	1.79
69	270	18.42	27.3	3.9	2.43
68	280	18.08	27.1	3.5	3.00
65	284	17.95	27.5	2.0	3.61
71	290	17.76	27.1	1.8	5.34
64	298	17.51	27.1	1.8	6.88

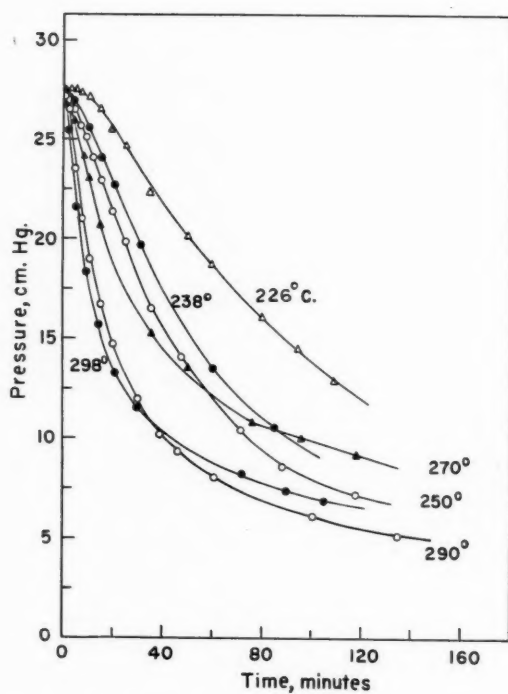


FIG. 8. Pressure as a function of time for reactions at different temperatures of acetylene containing about 0.7% oxygen.

The plot of $\log k$ against $1/T$ for these two series of reactions is shown in Fig. 9. An abrupt change of slope in the activation energy curves can be seen near 280°C . at the same place where a minimum is found in the pure acetylene curve. However, the curve is regular and follows the curve for the pure acetylene reactions over a certain region. The slope is much more pronounced for reaction temperatures beyond 280°C . but is parallel to the pure acetylene curve. The reaction products, for temperatures beyond 280°C ., were again mostly liquid hydrocarbons with a little cuprene, which was dark and quite dense.

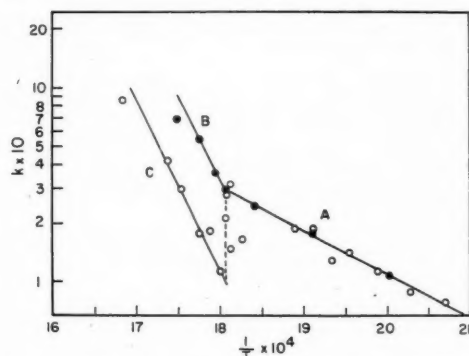


FIG. 9. Apparent activation energy. The black circles are for acetylene with approximately 0.7% oxygen; the open circles for pure acetylene.

In as much as the curves $\log k$ vs $1/T$ are straight lines, their slopes are a measure of the apparent activation energy of these reactions. These have been calculated and are given in Table V.

Whatever uncertainties are involved, it is clear that there is a discontinuity at about 280°C ., connected with a sudden fourfold increase in the apparent activation energy, both in the absence and presence of oxygen. Moreover, the velocities for the reactions without oxygen become erratic in the vicinity of that temperature. Since drawn metals have a tendency to undergo recrystallization at certain temperatures (3), the electrical resistance of the copper wire was measured from 200° to 300°C . but showed no discontinuity. Moreover, the same reaction velocity was found when copper wire preheated at

TABLE V
APPARENT ACTIVATION ENERGY

Reaction	Temp., $^\circ\text{C}$.	$-\Delta H_a$, kcal./mole
A (without oxygen)	210 - 280	10 ± 1.5
A (with oxygen)	210 - 280	10 ± 1.5
B (with oxygen)	280 - 300	40 ± 1.5
C (without oxygen)	280 - 300	40 ± 1.5

330° C. for one hour was used as catalyst instead of unheated wire. No indication that one of the copper oxides undergoes a transformation at 280° C. has been found in the literature. It seems, therefore, that the effect is not due to a change in the catalyst. Nor is the high-temperature reaction connected with a decomposition of the cuprene, for no detectable change occurred when cuprene grown at 230° C. was heated for long periods at 300° C. in a vacuum.

Side Reactions

A complete analysis of our data would involve quantitative measurements of the amounts of secondary products: residual gases, heavy hydrocarbons which are seen to distill in small quantities into the cool parts of the apparatus, and some carbon formed at the higher temperatures. The decrease in total pressure, as found in this work, is only an approximate measure of the amount of cuprene formed, since some of the acetylene is diverted to the production of other substances and some of the remaining pressure is due to the lighter products. If P_0 be the initial acetylene pressure, P the pressure at time t , and P_f the final pressure, then the pressure P_c of the acetylene which has been converted into cuprene and other nonvolatile products is

$$P_c = (P_0 - P) \left(1 - n \frac{P_f}{P_0} \right),$$

where n depends upon the average number of acetylene molecules required to form one molecule of volatile product. Since this correction is relatively small, unlikely to vary much between two reactions, involves an unknown factor, and does not account for the nonvolatile products, it seemed preferable, in this exploratory work, to establish direct comparisons between uncorrected data. For the same reasons and also because of the complex physical structure of the fibrous polymer revealed by electron microscopy (22, 23), a detailed kinetic analysis of the curves would be meaningless.

Discussion

The main conclusions from the kinetic data presented are: (1) the maximum velocity of the autocatalytic reactions shows a first-order dependence upon acetylene concentration, (2) the temperature coefficient changes abruptly at 280° C., indicating the emergence of a new process or mechanism, and (3) oxygen can exert two opposite effects, suggesting that it acts both on the catalyst and on the reaction itself.

From the linear dependence upon acetylene concentration it can only be concluded that acetylene probably adds itself monomolecularly to the growth centers, which are not saturated under the conditions of the reaction.

The break in the velocity-temperature curve and the modified aspect of the products above 280° C. indicate that two different and probably concurrent reactions must be considered. According to this view, the growth of cuprene with a low activation energy of about 10 kcal. per mole is predominant below 280° C., whereas the formation of liquid polymers becomes the faster reaction

above that temperature. The activation energy of 40 kcal. per mole found for this high-temperature reaction can be compared with that of 40.5 kcal. per mole reported by Pease (17) for the homogeneous thermal polymerization of acetylene between 420° and 450° C. It may be that the copper helps to initiate that thermal polymerization which then propagates at measurable velocities even at the much lower temperatures used in our experiments.

It would seem that oxygen affects the formation of the liquid more than that of the cuprene. If an adequate supply of this gas is available, the velocities of cuprene and liquid formation seem simply to add up, as suggested by Curve *B* (Fig. 9). However, if the reaction is dependent upon traces of oxygen presumably always present in the system, erratic velocities are obtained at the transition temperature, and the over-all rate of acetylene consumption is decreased (Curve *C*) as though the two reactions were impeding each other. The reason for the depressed position of Curve *C* may be that initiation of the liquid polymer is favored in the competition for oxygen, but that its growth consumes acetylene at a slower rate than would that of cuprene.

However, most of the effects reported in this work have been observed at or below 250° C. and are believed to reflect almost exclusively the behavior of the cuprene reaction. The apparent activation energy of about 10 kcal. per mole would be consistent with a limiting step involving free radicals (21) or some physical process such as sorption or migration on or in the solid phase. There is no evidence in favor of either possibility.

Since some oxygen will always be found in the system in the presence of the reducing acetylene, it is difficult to define the state of oxidation of the catalyst and to connect its activity with any of the species: copper, cuprous oxide, or cupric oxide, which are all known to act as catalysts. Although the enhanced activity of the preoxidized copper wire would seem to be due to one of the oxides, it may just as well result from a disintegration of the surface and its ability to yield finely dispersed copper upon reduction. An X-ray examination of our samples by Watson (23) shows that as long as cuprene is capable of further growth it contains minute amounts of copper and traces of cuprous oxide, whether copper or cuprite was used as the original catalyst. Incidentally, this suggests that growth occurs at the end of the fiber which is attached to the catalyst, minute particles of which are carried over in the seeding experiments. In such a process, there would be no reason to distinguish between initiation and growth. Concerning the identification of the catalytic species, it is possible that the activity resides in the interface between copper and cuprous oxide. It is known that solid-gas reactions, including the reduction of copper oxide (18), take place at the interface between the old and the new phase. The interface would first develop by the action of the acetylene on the thin oxide layer always present on copper, thus accounting for the autocatalytic character of the reaction. It is even possible that the geometrical restrictions imposed upon the propagation of such an interface may have something to do with the tubular form of the cuprene fiber.

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STUDIES OF THE MICROHETEROGENEITY OF POLYBUTADIENE AND GR-S¹

I. THE PROPAGATION MECHANISM IN THE POLYMERIZATION OF BUTADIENE

BY J. LONGFIELD, R. JONES, AND C. SIVERTZ

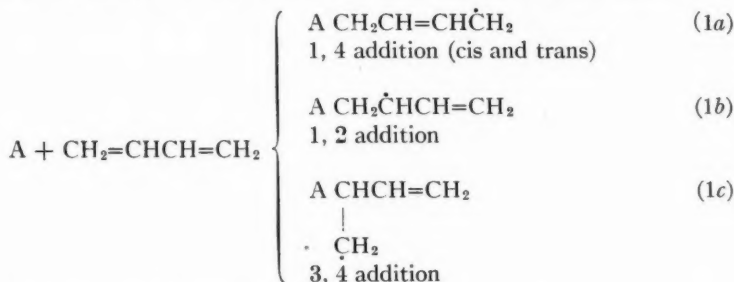
Abstract

When *n*-butyl mercaptan is reacted in a one to one ratio with butadiene in an emulsion system containing persulphate, crotyl *n*-butyl thioether is exclusively formed as the product of the initiation step. That is, no 1, 2 or 3, 4 addition was found for this step but only the 1, 4. Crotyl *n*-butyl thioether and methylvinylcarbinyl *n*-butyl thioether have both been synthesized and certain physical properties determined. It is concluded that in all free radical attacks upon butadiene, the terminal carbon is attacked. The resulting radical may or may not resonate between structures which yield 1, 4 addition and 1, 2 addition; for example, when a mercaptan radical attacks, the resonance is suppressed, but, when styryl or butadienyl radical attacks, the resonance results in the observed ratios of 1, 2, 1, 4 addition in polybutadiene and copolymers of butadiene and styrene. The nature of the products and the yield indicates that the overwhelming number of initiations are made by butyl mercaptan radicals and termination is almost exclusively made by mercaptan.

Introduction

The mechanism of the origin of the macroheterogeneity or distribution of molecular size is on a better experimental and theoretical foundation than the origin of the microheterogeneities. The latter comprise chiefly internal and external double bonds and *cis-trans* forms. This paper describes an experimental approach to the question of the mechanism of the origin of external double bonds and to some extent, *cis-trans* forms. The next paper, now in preparation, will describe an experimental approach to the mechanism of the formation of branches and cross links.

On the basis of structural considerations it might be expected that when a free radical, such as a growing polymer \dot{A} , attacks a butadiene molecule, the addition could take place in any one or all of the following three ways:—



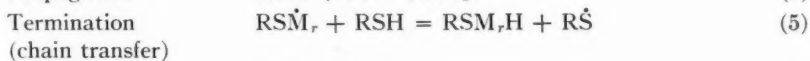
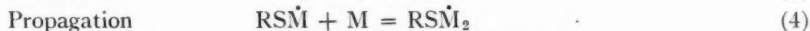
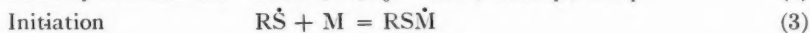
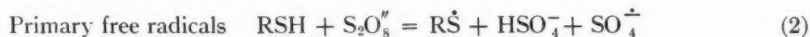
¹ Manuscript received March 11, 1950.

Contribution from the Department of Chemistry, Faculty of Arts, The University of Western Ontario, London, Ont.

appeared to us that it should be possible to produce polymers in an environment of mercaptan sufficiently strong to ensure that the propagation steps are practically suppressed and ensure a product which consists almost entirely of an initiation and termination step only. If the mercaptan employed has a low molecular weight, the resulting incipient "polymer" could be separated by methods of fractionation and should be easily characterized with respect to 1, 2 and 3, 4 and 1, 4 addition. Such a product might display all the microheterogeneities of the large polymer, and, if so, the effects of temperature and other variables on the occurrence of various structures could be more readily observed than on large polymers.

Experimental Procedure

It was decided to use emulsion polymerization with potassium persulphate as catalyst and *n*-butyl mercaptan as the modifier. In such a system the reaction mechanism is generally considered to be:



Previous work (8) indicated that if the mercaptan concentration be increased until it is approximately that of the monomer, the propagation step could be greatly reduced.*

Butadiene was employed as monomer and consequently the product RSMH would consist of any one or all of the following isomers of butylbutenyl thioether:

- | | |
|---|---------------|
| (1) $\text{RSCH}_2\text{CH}=\text{CHCH}_3$ | 1, 4 addition |
| (2) $\text{RSCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ | 1, 2 addition |
| (3) $\text{RSCHCH}=\text{CH}_2$ | 3, 4 addition |



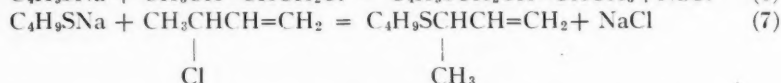
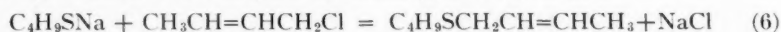
Thus it is apparent that these products may reflect all the structural modifications which would occur in the polymer and in a form which should make

* In a paper in preparation it is shown that the number average molecular weight of a polymer $\bar{M} = \beta \sum_{r=1}^{\infty} M_r (1 + \beta)^{-r}$, where r is the degree of polymerization and $\beta = \frac{k_{ct}(\text{RSH})}{k_p M}$, k_{ct} being the chain transfer velocity constant and k_p the propagation constant, and their ratio is the "transfer constant" C . For butyl mercaptan and butadiene this analysis gives $M = 89 + 54 \frac{1 + \beta}{\beta}$. In this laboratory C for the first step has been found to be about 6, hence for a ratio of mercaptan/monomer = 1 $\bar{M} = 89 + 54 \times \frac{7}{6}$. Thus a high yield of the initiation step product may be expected for such concentrations of mercaptan and monomer.

them separable by ordinary analytical methods. Further, it was hoped that the various isomers would occur in approximately the same ratio in the butyl butenyl sulphides as in the polymer.

After reacting the mercaptan-butadiene-persulphate mixture, which is described below under "Experimental Detail," two methods were employed for the identification of the possible isomers of the butyl butenyl sulphide. The first depends on separation of the products of polymerization by distillation and identification of the fractions. The second method involves cleavage of the sulphides with cyanogen chloride and identification of the resulting butenyl chlorides.

The 1, 4 addition product, crotyl *n*-butyl thioether and the 3, 4 addition product, methylvinylcarbinyl *n*-butyl thioether, were also prepared by direct synthesis by reacting sodium *n*-butyl mercaptide with the corresponding butenyl chlorides according to Equations (6) and (7) below.



These reactions were carried out under conditions which Roberts, Young, and Winstein (6) found were unfavorable to rearrangement in the analogous reaction to produce crotyl ethyl ether and methylvinylcarbinyl ethyl ether. Some physical properties found for these "synthesized" butyl butenyl thioethers are shown in Table I.

TABLE I
PHYSICAL PROPERTIES FOUND FOR THE "SYNTHESIZED" THIOETHERS

Property	Crotyl <i>n</i> -butyl thioether from 1-chloro-2-butene	Methylvinylcarbinyl <i>n</i> -butyl thioether from 3-chloro-1-butene
Molecular weight	143 ± 2	144 ± 2
Density, at 25°C.	0.8551	0.8758
Boiling point, °C.	186 (738 mm.)	170.5 - 171.5 (740 mm.)
n_D^{25}	1.4703	1.4623

Analysis by Fractional Distillation

The difference in boiling points is seen to be great enough to permit a satisfactory separation by distillation. At the time of writing, the 1, 2 addition product ($\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{SC}_4\text{H}_9$) has not been synthesized but its boiling point has been estimated to be 179°C. by a method which has been confirmed by giving close estimates for the other two thioethers.

About 500 cc. of the product of the "polymerization" reaction was separated by distillation at reduced pressures from the unreacted monomer and mer-

captan and then distilled in a Todd still containing about 30 equivalent plates. Only *one* isomer could be identified having the following physical properties.

TABLE II
PHYSICAL PROPERTIES OF THE THIOETHERS PRODUCED BY
EMULSION POLYMERIZATION

Property	Value
Molecular weight	144 \pm 2
Density	0.8550 (25.0°C.)
Boiling point, °C.	185–186 (740 mm.)
n_D^{25}	1.4700

These values correspond well with those found for crotyl *n*-butenyl thioether (Table I) which is the 1, 4 addition product. This result indicates that none of the 3, 4 addition product, methylvinylcarbonyl *n*-butyl thioether is present. Further, the absence of the 1, 2 addition product is indicated although somewhat less conclusively.

Analysis by Cyanogen Chloride Cleavage

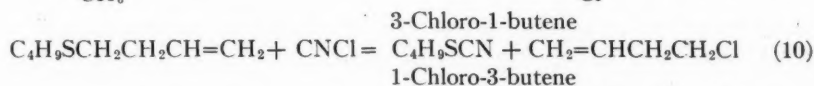
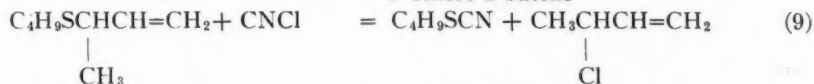
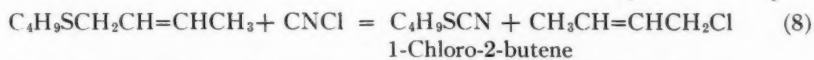
The reaction of organic sulphides with cyanogen bromide has been studied by Braun (1) who reports that when cyanogen bromide reacts with an unsymmetrical sulphide the following reaction occurs:



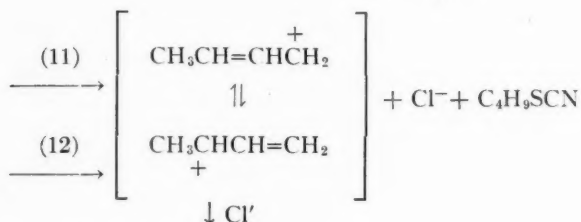
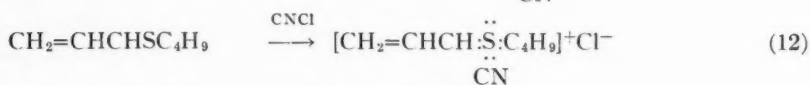
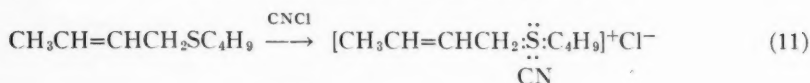
provided (1) R' is smaller than R,
(2) R' is unsaturated and R saturated,
(3) R' is a benzyl group and R aliphatic

The corresponding reaction with cyanogen chloride was employed to cleave the possible isomers of the butylbutenyl sulphides.

Assuming that no rearrangements take place, the following reactions may be expected:



However in the light of Young and Andrews' work (9) it might be expected that the cleavage would pass through an ionic stage and result in an allylic shift involving both the 1, 4 and 3, 4 isomers thus:—



finally $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$ and $\text{CH}_2=\text{CHCHCH}_3$ are produced.



This mechanism was confirmed by cleaving the synthesized 1, 4 product with cyanogen chloride and showing by distillation that both 3-chloro-1-butene and 1-chloro-2-butene were produced (7).

Thus as a result of the preceding mechanism we can expect a mixture of crotyl *n*-butyl thioether and methylvinylcarbinyl *n*-butyl thioether or either one *alone* to yield a mixture of 1-chloro-2-butene and 3-chloro-1-butene. On the other hand *any* 1, 2 addition product should yield 1-chloro-3-butene only.

On reaction of equimolar quantities of cyanogen chloride with the thioethers which were produced in emulsion polymerization, and subsequent fractionation of the butenyl chlorides resulting from cyanogen chloride cleavage, only two of the three possible chlorobutenes were found; these were 1-chloro-2-butene (*ca.* 73%) and 3-chloro-1-butene (*ca.* 27%) which, as pointed out, could result from either the 1, 4 or 3, 4 addition product. No trace was found of the 1-chloro-3-butene or of any *n*-butyl chloride which might have resulted from a "reverse" scission of the sulphide.

General Conclusions

The results of the cleavage confirm the fractionation data regarding the absence of any 1, 2 addition product, and we have seen that the presence of 3-chloro-1-butene does not indicate the presence of methyl vinyl carbinyl thioether, since it could have resulted from crotyl *n*-butyl thioether by a reaction involving an allylic rearrangement.

These facts lead one to conclude that the sulphide formed in the polymerization system is, within the accuracy of the analysis (*ca.* 5%), *all* crotyl *n*-butyl thioether, i.e., the 1, 4 addition product. There is no indication of any 1, 2 or 3, 4 addition product. Furthermore, the results of experiments on the relative

reactivities of the two thioethers in a polymerization mix such as was used indicate that one cannot account for the complete absence of these vinyl compounds by assuming a preferential attack by mercaptan free radicals during the reaction (see Experimental Detail below). We may therefore conclude that in the polymerization system used, the initiation step results in the addition of the 1, 4 type only, with no additions of the 1, 2 or 3, 4 types.

However, polybutadiene and GR-S are known to have side vinyl groups and therefore the propagation steps cannot involve 1, 4 addition only. Thus we are forced to the conclusion that the initiation step and the propagation step do not necessarily proceed by identical mechanisms. This in turn means that the structural heterogeneity of the butenyl butyl thioethers is *not* representative of the microheterogeneity of the polymer, since the mechanism of the initiation step is not that by which the bulk of the polymer is formed.

This being the case it may be possible to investigate from the same point of view the next higher "polymer", that is, the molecules resulting from one initiation step, one propagation step, and a termination step. Assuming that all the initiation proceeds by 1, 4 addition, these octadienyl *n*-butyl thioethers in turn would consist of three possible isomers resulting from 1, 4, 1, 2, and 3, 4 addition. In this connection it might be expected that the attack of an RSM radical would be more representative of the polymerization step than is the attack of an R \dot{S} radical, and consequently the analysis would be more useful in an elucidation of the propagation mechanism. However, it has since been shown in this laboratory that the transfer constant for butadiene appears to increase in the first few additions. This means that the influence of the R \dot{S} group is propagated beyond the first addition. Hence it is not likely that even the addition product including two monomers would be characteristic of the larger polymers.

The Origin of 1, 2 Addition

The experimental evidence presented above shows that an R \dot{S} radical does not attack an internal carbon atom in butadiene. Moreover in subsequent studies in this laboratory of the addition of R \dot{S} radical to 1-pentene no product except that corresponding to addition to the 1-carbon has been observed. These facts are in accord with the expectation that a free radical will attack the region of highest electron density.

It seems, therefore, reasonable to conclude that a styryl or butadienyl radical will behave in the same way. If this is true then 1, 2 addition must result from the resonance as suggested by Flory (2). Analyses of the double bonds in polybutadiene show that between 25 and 30% are external. We may then conclude that for the conditions of the syntheses involved the unpaired electron spends about this percentage of the time in the 2-position.

In the cleavage of the butenyl thioethers we have seen, in Equations 11 and 12, that a similar resonance, in an ionic form, accounts for the experimentally found 1-chloro-2-butene and 1-chloro-3-butene. It appears more than a co-

incidence that the product of this resonance results in about 27% of the 1-chloro-3-butene, which corresponds to the 1, 2-addition resonance. Closer analysis of these two resonances, namely the free radical and ionic, leads one to expect that they might very well result in about the same equilibrium, at comparable conditions, since the presence of the charge in the latter can be expected to make the same energy contribution to each state of the electron and hence result in the same relative probabilities for each state in both cases. It would then appear that in a resonance of the type shown in (11) and (12) we have a very close model of that which occurs in the butadienyl radical when it is removed from the influence of the initiator. This suggests that a study of the products of such a cleavage reaction as a function of temperature, should reveal the same trend as that observed with 1, 2 and 1, 4 addition in GR-S.

Experimental Detail

Synthesis of Butyl Butenyl Sulphides by Emulsion Polymerization

The recipe used in the synthesis of the butenyl sulphides is shown in Table III.

TABLE III
REACTION MIXTURE FOR PREPARATION OF ADDITION PRODUCT

Reagent	Moles	Wt. (gross)	Volume, ml.
2.5% Orvus soln.*		60	60
Butadiene	0.37	20	31
n-Butyl mercaptan	0.37	34	40
Potassium persulphate	0.026	6	

* Lauryl sulphate.

The quantities of reagents shown in the above table were placed in a six ounce bottle and allowed to react with constant stirring for 20 hr. at 50°C. The reaction period of 20 hr. may not be significant, since at the end of this time the emulsions were always broken. After the reaction was complete, the oil and water layers were separated. The oil layer was then dried and subjected to fractional distillation.

Fractionation of the Oil Phase

Through the co-operation of Polymer Research and Development Division a fractionation of a large batch of the oil phase resulting from the syntheses was performed in a Todd still. The following data were obtained.

Cut No. 2 is largely unreacted butyl mercaptan.

Cut No. 4 was refractionated and found to consist of a small amount of butyl mercaptan and a product boiling at 185–186°C.

Refractionation of Cut No. 3 indicated it to be a mixture of butyl mercaptan and the 186° boiling product. There was no indication of any compound boiling at a temperature between 98° and 186°C.

TABLE IV
FRACTIONATION OF OIL PHASE RESULTING FROM
EMULSION POLYMERIZATION

Cut No.	Still head Temperature, °C.	Weight of fraction, gm.
1	20-94	Trace only
2	94-100	366
3	100-183	95
4	183-186	316
Residue (polymer)	—	110

Reaction of Butyl Butenyl Sulphide with Cyanogen Chloride

Cyanogen chloride (0.9 mole) was added to butenyl sulphide (0.9 moles) and the solution sealed in a reaction vessel and allowed to react for 5 1/2 hr. at 70°C. After this reaction period the mixture, which was a dark reddish-brown in color, was subjected to fractional distillation. The fractionation yielded four fractions consisting chiefly of (1) unreacted cyanogen chloride, (2) butenyl chloride, (3) unreacted butenyl sulphide, and butyl thiocyanate, and (4) residue (undetermined). Refractionation of the crude butenyl chloride yielded two fractions whose properties are listed in Table V.

TABLE V
PHYSICAL PROPERTIES OF CHLOROBUTENES

Compound	Boiling point, °C.		Refractive index, n_D^{25}	
	Literature (3, 9)	Experimental	Literature (3, 9)	Experimental
3-Chloro-1-butene	63.5	63.0-64.0	1.4128	1.4125-1.4128
1-Chloro-2-butene	84.0	84.0	1.4328	1.4325-1.4328

Evidently the two butenyl chlorides isolated are 1-chloro-2-butene and 3-chloro-1-butene. There is no evidence, either in the boiling point or refractive index data, of the presence of any 1-chloro-3-butene, the physical constants of which are also given in the literature (3, 9).

Reactivities of the Thioether Isomers

Equimolar quantities of crotyl *n*-butyl thioether, methylvinylcarbinyl *n*-butyl thioether and *n*-butyl mercaptan were emulsified in a 2.5% solution of "Orvus" containing 10% by weight of potassium persulphate. This duplicates the environment to which the thioethers are exposed during the polymerization reaction. The emulsion was placed in a sealed bottle and the latter rotated end over end in a 50° bath for 28 hr. Then the oil phase was separated and fractionally distilled.

By this distillation, 89 mole % of the mercaptan, 90 mole % of the crotyl *n*-butyl thioether (1, 4 addition) and 76 mole % of the methylvinylcarbinyl *n*-butyl thioether (3, 4 addition) were recovered unchanged. The data indicate that the 3, 4 thioether is attacked more readily than the 1, 4 thioether. However, the over-all disappearance of thioethers through the attack of mercaptan is relatively small even over this prolonged period (28 hr.), so that even a considerable differential in rate of attack could have very little effect on the composition of the thioether mixture produced by a polymerization reaction.

Acknowledgment

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STUDIES ON THE SURFACE AREAS OF CADMIUM AND COPPER, AND THE MECHANISM OF CADMIUM POLARIZATION¹

BY J. M. ROXBURGH AND C. A. WINKLER

Abstract

The areas of mechanically cleaned cadmium electrodes, measured by rate of build-up of hydrogen overvoltage, have been shown to decrease with time of immersion in air-free acid solutions. The relative rate of decrease did not depend upon acid concentration in excess of 10^{-2} molar, nor upon passage of current or initial area, but exposure to air accelerated the decrease in area. The measured area was shown to depend upon the current used for the measurement, particularly with electrodes of large areas. Copper electrodes did not show the effects observed with cadmium. Cadmium polarization was shown to be linearly related to current, and independent of the measured area. This indicates that concentration polarization is operative in the deposition of cadmium.

Introduction

A previous publication from this laboratory (6) described the construction and operation of an apparatus, involving the use of a cathode ray oscillograph, for determining the active surface area of an electrode from measurements of the rate of build-up of hydrogen overvoltage (2). The present paper gives the results obtained with this apparatus in a study of the effect of certain factors on the measured surface areas of cadmium and of copper, and of the mechanism of cadmium polarization.

Experimental

Apparatus and Materials

Except for the electrolytic cell, the apparatus used was identical with that described in the previous paper (6). For present purposes, the more convenient cell shown in Fig. 1 was constructed from two 300 cc. flasks. Each compart-

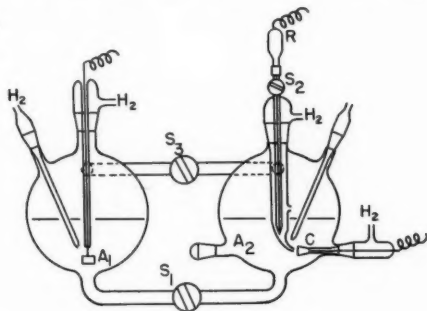


FIG. 1. Diagram of cell.

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.

ment was fitted with an inlet to bubble hydrogen through, or pass hydrogen over the electrolyte. Provision was also made for a platinum anode at A_1 for surface area measurements, and a cadmium or copper anode at A_2 for deposition experiments. The cathode was at C and a calomel probe electrode at R . During surface area measurements, stopcock S_1 was closed to prevent diffusion of oxygen, released from the anode, into the cathode compartment. Electrical contact between compartments was through the film of electrolyte wetting the stopcock.

Cadmium and copper cathodes were mounted as described previously (6), the cadmium being of "Tadanac" brand (Consolidated Mining and Smelting Co., Trail, B.C.) and the copper of electrolytically refined stock.

The water, sulphuric acid, cadmium sulphate, and hydrogen were purified as in the earlier study. Solutions were stored in Pyrex flasks arranged to permit deaeration with hydrogen and transfer of the solutions to the cell through "Tygon" tubing without coming into contact with air.

Procedure

Operation of the apparatus differed in only one respect from that described in the earlier paper. In the present study it was found more reliable and faster to determine the slope of the overvoltage build-up curve on the oscillograph screen from repeated visual observations on several sweeps, rather than from a photograph of a single sweep.

Results and Discussion

Change in Area of Cadmium Electrodes

The surface of the cathode was modified, as desired, by grinding off simultaneously the metal and glass surrounding it on coarse or fine emery cloth, or with emery powder and water on a glass plate. Choice of grinding material enabled widely different electrode surface areas to be obtained, the order of magnitude of the area being predictable from the method of grinding, or "cleaning", employed.

Measurements were made of the electrode areas initially and after aging for six hours in air-free $N/5$ sulphuric acid, hydrogen being bubbled through the solution, and current being passed, in the interval between measurements. Potentials of the electrodes, relative to the calomel half-cell, were also determined using a Leeds and Northrup type K potentiometer, the amplifier, bias battery, and main current supply battery being disconnected. The experimental conditions for and results of the measurements are shown in Table I. Smaller measured areas and more negative potentials of the electrodes after aging are quite evident, particularly for the electrodes of largest initial areas.

The more negative electrode potentials recorded after aging an electrode (Table I) might be partially the result of removing oxide from the electrode surface, but it is also possible, even probable, that a more negative potential

TABLE I
EFFECT OF AGING ON AREAS AND POTENTIALS OF CADMIUM
ELECTRODES

Apparent electrode area, 0.4 cm² Electrolyte, *N*/5 air-free sulphuric acid

Electrode treatment	Measuring current amp. $\times 10^{-6}$	Measured area (\times planar)		Potential (vs. sat. calomel)	
		Initial	After 6 hr.	Initial	After 6 hr.
Coarse emery cloth	6.5	6.2	2.0	-0.757	-0.768
" " "	6.5	10.0	2.1	-0.753	-0.761
" " "	6.6	—	2.7	-0.747	-0.758
" " "	6.4	9.8	2.4	-0.760	-0.759
Coarse, followed by fine, emery cloth	6.5	25.5	5.5	-0.740	-0.770
	6.5	13.3	4.1	-0.751	-0.753
	6.5	24.0	4.0	-0.741	-0.772
	6.5	22.4	4.8	-0.750	-0.765
Emery powder and water	6.7	1500	83	-0.715	-0.763
	8.2	—	260	-0.700	-0.769
	6.7	970*	330	-0.710	-0.767

* After one hour.

is associated with a more stable surface condition of the electrode. More detailed evidence for this is presented in a subsequent paper.

To determine, if possible, the cause of the observed decrease in electrode area with aging, a study was made of the change in surface area of cadmium cathodes cleaned with coarse emery cloth and subsequently treated in one of the following ways, the electrolyte in all but the last being *N*/5 sulphuric acid:

- Current flowing (6.5×10^{-5} amp.) throughout experiment.
- Current not flowing between measurements of area.
- Solution forced back into anode compartment between area measurements; electrode in hydrogen gas but wet with electrolyte.
- Dry electrode stored in hydrogen gas for 12 hr. between cleaning and immersion in acid for measurements of area.
- Current flowing throughout experiment but electrolyte renewed after three hours.
- Electrodes immersed in air-free redistilled water, one for three hours, two for 18 hr., between cleaning and immersion in acid for area measurements.
- Electrode immersed in *N*/5 potassium sulphate solution for three hours prior to immersion in acid for area measurements.
- Electrolyte, phosphoric acid of hydrogen ion activity approximately equivalent to *N*/5 sulphuric acid.

Measurements of surface areas were made throughout with a current of 6.5×10^{-5} amp.

In Fig. 2 are plotted some of the results from these experiments, sufficient to show that the area decreased at approximately the same relative rate with all the different electrodes under the variety of conditions. To provide a basis of comparison, the ordinates in this figure represent values of the measured areas as multiples of the final area. Results from some 20 additional experiments are not shown, since they merely confirmed the behavior shown in Fig. 2.

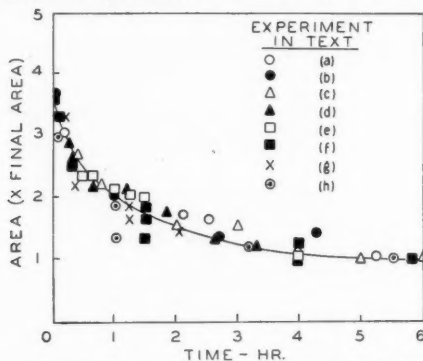


FIG. 2. Change of area with time of cadmium electrodes at 20°C.

Apparently, storage of the dry electrode in hydrogen gas or immersion of it in redistilled water or potassium sulphate solution caused no significant change of area. Subsequent immersion in the acid electrolyte, however, resulted in the usual marked decrease of area.

If a short initial period of very rapid change in area is disregarded, a linear relation (c.f. Fig. 3) between $\log (A_t - A_f)$ and time may be obtained for any electrode under any condition of change, where A_t is the measured area at time t and A_f is the final area (taken here as the area after six hours, beyond which time no further significant change of area occurred).

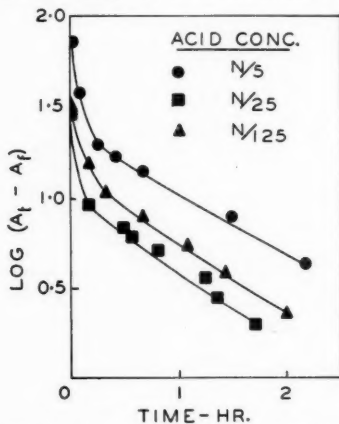


FIG. 3. Effect of acid concentration on change of area with time of cadmium electrodes in air-free sulphuric acid at 20°C.

The effect of hydrogen ion concentration of the electrolyte on the rate of change of electrode area was determined in $N/25$ and $N/125$ sulphuric acids, area measurements being made, as before, with a current of 6.5×10^{-5} amp. In Fig. 3 are plotted some typical results. It will be noted that the slopes of the linear portions of the curves are roughly comparable. Over some 200-fold change in $(A_t - A_f)$ and with no apparent relation to acid concentration, the slope was found to vary from approximately 0.25 to 0.40 at 20°C ., with an average value at this temperature of about 0.3. Experiments at 40°C ., in $N/5$ air-free sulphuric acid, gave the same type of relation between $\log(A_t - A_f)$ and time, but the average slope of the linear portion of the curves was 0.6. If it is assumed that the average slopes are proportional to the rate constants at the two temperatures for the rate governing step in the reactions responsible for the change in electrode area, an activation energy for this step of roughly 7 kcal. may be calculated.

The effect of exposure to air on the rate of decrease of measured area is shown by some typical curves in Fig. 4. In these experiments the electrode was removed from the cell after some time in the electrolyte ($N/5$ air-free sulphuric acid), dried, and left in air for one minute. When returned to the cell the electrode had the same area as immediately before it was removed, but the subsequent decrease in measured area was accelerated temporarily.

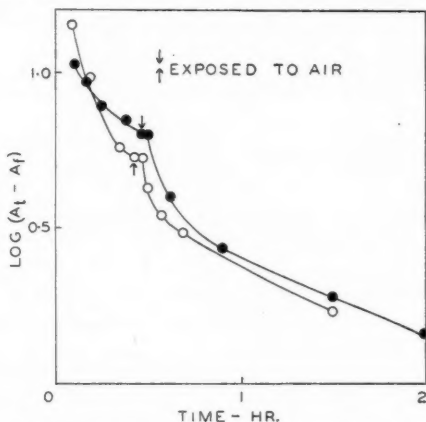


FIG. 4. Effect of exposure to air on the rate of change of area of cadmium electrodes.

The observed decrease in measured area of cadmium electrodes in the presence of acid presumably corresponds to a reduction in the number of active centers at which hydrogen deposition can occur. This apparently results from solution of those portions of the electrode which are most active and contribute a large proportion of the true area, followed perhaps by redeposition in a more stable condition. Since the rate at which the area decreased was essentially independent of acid concentration over a considerable range, the rate of the reaction responsible for the change in area would appear to be controlled by

diffusion of cadmium ions away from the points of attack. The observed activation energy of about 7 kcal. would be appropriate to a diffusion controlled process.

The accelerating effect of exposure to air might be explained by assuming that oxygen removes part of a protective "hydride" layer (4), thus increasing the area available for attack by acid.

Change in Area of Copper Electrodes

Experiments were made with copper electrodes to obtain some indication of the possible generality of the behavior observed with cadmium. Copper was selected because its properties are somewhat similar to those of cadmium but its electrode potential, relative to the normal hydrogen electrode, is of opposite sign to that of cadmium. The results of these experiments may be summarized briefly.

The largest electrode areas attainable with copper, by grinding with emery and water, were 60 to 65 times planar (c.f. cadmium, at least several hundred times planar). Such copper electrodes showed a comparatively small decrease in area to about 45 times planar after two hours aging in $N/5$ sulphuric acid, beyond which time no further change occurred. When the electrode areas were less than about 25 times planar initially, no significant decrease of area occurred on aging in the electrolyte for 20 hr.

Bubbling air through the electrolyte or exposing the clean electrode to air increased the measured area (e.g., from 16 times planar to 24 times planar after 10 min. exposure) but passage of a current of air for 10 min. reduced the area again, generally to a value approximately the same as that which prevailed prior to oxidation. The decay time for hydrogen overvoltage on copper (from the oscillograph trace after switching off the current) was reduced from a value of 10 to 15 min. on an unoxidized surface to as little as 10 sec. on an oxidized surface. With cadmium, the return of the electrode potential to the value measured at zero current was always of the order of a few seconds.

In area measurements with cadmium, the presence of small amounts of cadmium ion in the electrolyte resulted in an S-shaped trace on the oscillograph (5). With copper, the presence of copper ion in the electrolyte appeared not to alter the shape of the trace, although its slope was markedly increased (one experiment).

Influence of Current on the Measured Areas of Cadmium Electrodes

During the preceding measurements of area, occasional minor variations in the current used for measurement gave some indication that the measured area depended upon the measuring current. A study of this variation was made, using three cadmium electrodes of which the areas measured with a current of 10^{-4} amp. were 2, 27, and 156 times planar. These electrodes, initially of larger surface areas, were aged in electrolyte to attain essentially stable

values of the surface areas measured with given current. The results are plotted in Fig. 5, where the ordinates represent percentages of the areas measured with a current of 10^{-4} amp. It will be noted that, as the current is decreased, the measured area increases rapidly.

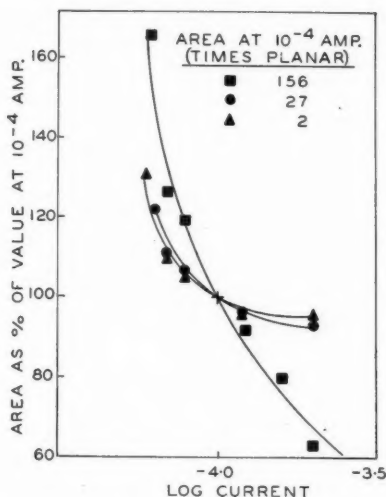


FIG. 5. Effect of current on the measured area of cadmium electrodes.

In view of this behavior, an extended investigation would seem to be necessary to define the conditions for measurement of an area in absolute terms by the Bowden-Rideal method, if indeed it is possible at all. Meanwhile, there appears to be no serious objection to using the method for determining relative areas, or relative changes of area with a given measuring current as in the present investigation. With smaller measured areas, up to about 25 times planar, the error in such relative measurements is probably less than 5%. With larger measured areas such as 100 to 150 times planar, where the error may be 15 to 20%, the larger possible error does not obscure the essential conclusions. Practically all of the present studies were made with areas less than 70 times planar, measured at 6.5×10^{-5} amp.

The increase in measured area with decrease of current used for the measurement might be accounted for if minute fissures on the surface were available to hydrogen at low currents while at higher currents the concentration of hydrogen ion in such fissures could not be maintained by diffusion. Such an interpretation agrees with the observation that the effect of current on the measured area is less, the smaller the electrode area. It is interesting to note that with a planar mercury surface, the capacitance of the double layer has been found independent of current density over the range 5×10^{-5} to 5×10^{-3} amp. per cm^2 (1).

Effect of Electrode Area on Cadmium Polarization

Three experiments were made, with cadmium electrodes of widely different areas, to determine the relation between current density and cadmium polarization, and the effect of electrode area on this relation. The electrodes used had relative areas of 2, 50, and about 8000 times planar, measured with a current of 6.5×10^{-8} amp. Cadmium polarization values were determined in air-free $N/1$ cadmium sulphate: $N/10$ sulphuric acid electrolyte, using a type K potentiometer.

The results for these experiments are shown in Fig. 6, from which it is evident that the cadmium polarization is independent of the electrode area available to hydrogen, and depends only on the current within the range studied. Such complete lack of dependence of the polarization on electrode area leaves little doubt that the cause of the polarization resides in the electrolyte, i.e., that concentration polarization prevails almost exclusively. This conclusion receives indirect support from studies on the effect of temperature (8), agitation (8), and addition of ammonium ion (3, 7) on the characteristics of cadmium deposits.

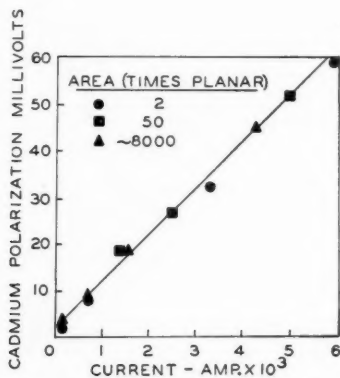


FIG. 6. Cadmium polarization - current relation for electrodes of different measured areas.

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POTENTIAL OF CADMIUM IN SULPHURIC ACID¹

BY J. M. ROXBURGH AND C. A. WINKLER

Abstract

The potentials determined for mechanically cleaned cadmium electrodes in air-free sulphuric acid electrolyte were less negative than those reported for deposited electrodes. Cleaning under air-free conditions did not remove this difference. It appears that the physical condition of the electrode surface affects the potential.

Introduction

In the course of studying the behavior of cadmium electrodes under various conditions (3, 4) it was observed that the potential, in air-free sulphuric acid, of mechanically cleaned or deposited cadmium electrodes was less negative than the value for deposited electrodes reported by Gatty and Spooner (1). Attempts to obtain a value in accord with theirs gave the results reported below.

Experimental and Results

The potential of the cadmium electrode *C* was measured relative to a calomel electrode *R* in a small cell of the type shown in Fig. 1, or in a larger cell described elsewhere (3), using a type K Leeds and Northrup potentiometer. In the smaller cell, the electrode could be cleaned, while it remained in position, by inserting a steel tool through the opening that normally carried the reference electrode. A cadmium plug, machined to fit tightly into a female ground joint, furnished the electrode. A slight hydrogen pressure (6 cm.) behind the electrode prevented seepage of electrolyte between the metal and glass, while a side arm allowed the cell to be swept with purified hydrogen before and during each experiment.

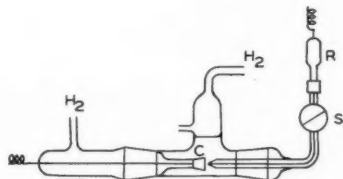


FIG. 1. Diagram of cell.

The hydrogen, water, and sulphuric acid were purified as in the previous study (3). Potassium chloride was repeatedly recrystallized from conductivity water. All solutions were carefully cleared of dissolved oxygen by prolonged (12 to 24 hr.) bubbling with purified hydrogen, and were transferred to the cell through "Tygon" tubing without coming into contact with air.

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.

In Table I are recorded the potentials of cadmium electrodes cleaned mechanically, and after exposure to air. The value of -0.753 v. for a freshly scraped surface is to be compared with the value of -0.81 v. reported by Gatty and Spooner (1) for a deposited cadmium surface in $M/20$ air-free sulphuric acid. Exposure to air for less than six minutes had no permanent effect on the potential but attainment of the final value was somewhat slower.

TABLE I
POTENTIAL OF CADMIUM ELECTRODE IN
 $N/5$ AIR-FREE SULPHURIC ACID AT 20°C .

Nature of surface	Average potential (relative to sat. calomel)*	Remarks
(a) Freshly scraped with steel bottoming tool in hydrogen.	-0.753 (4 expts.)	Decreases from about -0.760 v. to this steady value in $1/2$ hr.
(b) Surface (a) exposed to air for three minutes.	-0.751 (3 expts.)	About $1/2$ hr. required to recover from initial potential of about -0.720 v.
(c) Surface (b), after recovery, exposed to air for six minutes.	-0.751 (3 expts.)	Somewhat longer than $1/2$ hr. required to recover this potential.
(d) Surface (c), after recovery, exposed to air for 12 min.	-0.710 to -0.725 (3 expts.)	Not reproducible potential

* Value when potential did not change more than 1 mv. in five minutes.

Several experiments in the larger cell (3) gave results of which those shown in Table II are typical.

TABLE II
POTENTIAL OF CADMIUM ELECTRODE IN $N/5$ AIR-FREE
SULPHURIC ACID AT 20°C .

Time	Potential with current off, v.	Conditions prevailing since previous measurement
0	-0.758	Freshly cleaned with steel bottoming tool in air, no current passed, solution not stirred
10 min.	-0.772	Solution stirred
25 min.	-0.754	Solution not stirred
95 min.	-0.759	Solution stirred
115 min.	-0.754	Solution not stirred
150 min.	-0.754	Solution stirred
180 min.	-0.752	Solution not stirred
200 min.	-0.752	Solution stirred
380 min.	-0.783	Current passed, 10^{-4} amp. for 3 hr., solution stirred
440 min.	-0.775	Current off, solution stirred
25 hr.	-0.769	Current off, solution stirred
27 hr.	-0.779	Current passed, 2×10^{-3} amp. Solution stirred
27 hr., 10 min.	-0.761	Current passed, 2×10^{-3} amp. Solution stirred
27 hr., 45 min.	-0.761	Current passed, 5×10^{-3} amp. Solution stirred
28 hr.	-0.757	Current passed, 2×10^{-3} amp. Solution stirred

The potential in the stirred solution was more negative than that in the unstirred solution during the first two hours; this indicated establishment of steady state conditions between the electrode and solution during this time. Passage of current made the potential more negative, but the value never attained that reported by Gatty and Spooner.

Experiments were made with cadmium, silver, and lead electrodes in potassium chloride solutions to determine whether differences in experimental techniques were in some way responsible for the consistently less negative potentials for cadmium. The cadmium electrode was cleaned with a steel bottoming tool, the silver electrode with nitric acid, and the lead electrode was cut from the end of a wax covered rod of the metal (2). The results for these systems are given in Table III.

TABLE III

POTENTIALS OF CADMIUM AND SILVER IN *N*/1 AIR-FREE POTASSIUM CHLORIDE SOLUTION, AND OF LEAD IN AERATED *N*/1 POTASSIUM CHLORIDE SOLUTION AT 20°C.

System	Average potential, v.	Other workers	Remarks
Cd in <i>N</i> /1 air-free KCl solution	-0.781 (3 expts.)	-0.81 (1)	History of the electrode is important and affects the time taken to reach steady value
Ag in <i>N</i> /1 air-free KCl solution	-0.093 (3 expts.)	-0.015 (1)	Several hours to reach steady potential.
		-0.056 (2)	Stirring affects potential until steady value attained
Pb in <i>N</i> /1 aerated KCl solution	-0.503 (3 expts.)	-0.506 (2)	Steady value reached overnight

From the results in Table III, it seems reasonable to conclude that the zero potentials measured for cadmium are consistently less negative than the value obtained by Gatty and Spooner because of differences in the electrode surfaces rather than the method of measurement. While oxide film on the electrode would result in a less negative potential (1, also Table I), it does not seem likely that this would explain the whole difference, since the potentials of electrodes cleaned mechanically in the presence of hydrogen were not more negative than those cleaned in air. On the other hand, the more negative potentials obtained with deposited surfaces indicate that the potential of cadmium in air-free sulphuric acid may depend significantly on the method of preparation used.

Acknowledgment

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THE REACTIONS OF METHYL RADICALS WITH CYCLOPROPANE, ETHYLENE OXIDE, METHANOL, AND DIMETHYL ETHER¹

BY M. K. PHIBBS AND B. DEB. DARWENT

Abstract

The reactions of methyl radicals, produced by the photochemical decomposition of dimethylmercury, with cyclopropane, ethylene oxide, methanol, and dimethyl ether have been investigated between 100° and 250°C. The following activation energies (kcal. mole⁻¹) for the abstraction of hydrogen from the compounds by methyl radicals were found: cyclopropane, 10.2; ethylene oxide, 9.6; methanol, 8.2; and dimethyl ether, 8.0. The probability factors have been shown to be about 10^{-4} for all the compounds investigated.

Introduction

It has been shown by H. S. Taylor and his coworkers (2, 11) that the photolysis of dimethylmercury serves as a useful source of methyl radicals, and they have been able to obtain the activation energies of the reactions between this radical and several organic molecules. The present work is an extension of their technique to the four substances dimethyl ether, methanol, ethylene oxide, and cyclopropane, which were of interest to us in connection with other work.

Experimental

The dimethylmercury was prepared by the method of Gilman and Brown (4) and stored over fused calcium chloride. The methanol was a reagent grade Brickmann and Company product. The other substances were obtained in gas cylinders from the Mattheson Company, Rutherford, N.J. All reactants were thoroughly degassed and further purified by bulb to bulb distillation and retention of a middle fraction.

The experimental procedure outlined in references (2) and (11) was followed with only minor modifications. The reaction vessel was a quartz cylindrical cell 10 cm. long and 5 cm. in diameter. It was enclosed in a cylindrical furnace provided with quartz windows. The temperature was regulated by hand and maintained within 1°C. during a run.

The light source was a Hanovia (Type S-500) Hg lamp emitting, among other lines, the reversed 2537 Å line. The light was made approximately parallel by a suitably placed quartz lens. The cross-sectional area of the incident beam, and thus the quantum input to the cell, could be altered by means of a circular aperture of variable diameter between the lens and the cell. An ultraviolet photometer at the far end of the furnace showed that the light intensity reached a steady value about five minutes after the lamp was switched on. The run

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was started 10 min. after the cell was placed in the furnace and the lamp turned on. This allowed sufficient time for the furnace and cell to reach thermal equilibrium and for the lamp to attain its steady output. Care was taken to ensure that the cell occupied the same position in the furnace for all runs.

The analyses for methane and ethane were made in a Ward still (14). In some of the experiments the noncondensable gas was found to contain hydrogen and carbon monoxide; in these cases the methane was determined as a residue after oxidation of carbon monoxide and hydrogen on hot copper oxide. In all runs, the reaction vessel contained 50 mm. of dimethylmercury and 200 mm. of the other reactant.

Results

The effect of increasing temperature on the rates of formation of methane and ethane from the four compounds investigated is shown in Table I. These results show that the rate of formation of methane, with all four compounds, increases markedly with increasing temperature. The rate of formation of ethane differs significantly between the compounds investigated; it is approximately independent of temperature with cyclopropane and ethylene oxide but decreases with increasing temperature in the cases of methanol and dimethyl ether. This temperature dependence of the rate of formation of ethane indicates a temperature dependence of the stationary concentration of methyl radicals. Experiments in the dark, the results of which are included in Table I (*d*), show that comparatively little methane is formed as the result of the thermal decomposition of dimethylmercury in the presence of dimethyl ether at 250°C. No ethane was detected in the products of the thermal reactions. The effect of increasing the light intensity, by a factor of about 30, on the rates of formation of methane and ethane at different temperatures was investigated and the results included in Section (*d*) of Table I.

TABLE I

THE EFFECT OF TEMPERATURE ON THE PHOTOCHEMICAL DECOMPOSITION OF DIMETHYLMERCURY
IN THE PRESENCE OF ORGANIC COMPOUNDS
Volume of reaction vessel—200 cc. (approx.)

Expt. No.	Duration, hr.	Temp., °K.	Rate, cc. hr. ⁻¹		$\frac{\text{CH}_4}{\text{C}_2\text{H}_6}$
			CH ₄	C ₂ H ₆	
(a) Ethylene oxide					
5	4	373	0.027	0.349	0.0456
10	4	373	0.027	0.286	0.0505
6	4	423	0.178	0.391	2.284
7	2	473	0.488	0.368	0.806
8	1	523	1.013	0.317	1.79

TABLE I—Continued

Expt. No.	Duration, hr.	Temp., °K.	Rate, cc. hr. ⁻¹		$\frac{\text{CH}_4}{\text{C}_2\text{H}_6}$
			CH ₄	C ₂ H ₆	
(b) Cyclopropane					
1	4	373	0.016	0.454	0.0236
2	4	423	0.065	0.466	0.095
3	2	473	0.433	0.432	0.660
5	2	473	0.323	0.440	0.733
6	2	473	0.309	0.453	0.681
4	1	523	0.692	0.392	1.11
(c) Methanol					
5	4	373	0.093	0.383	0.150
4	4	423	0.288	0.310	0.516
1	2	473	0.662	0.221	1.405
2	1	523	1.341	0.132	3.68
3	1	523	1.288	0.134	3.52
(d) Dimethyl ether					
52	4	373	0.121	0.274	0.230
59	4	373	0.163	0.312	0.291
46 (a)	4	373	0.309	1.634	0.242
51	4	423	0.343	0.248	0.689
58	4	423	0.406	0.250	0.812
42 (a)	4	423	1.192	1.428	0.992
49	2	473	0.843	0.173	2.03
57	2	473	1.114	0.146	2.92
38 (a)	2	473	2.83	1.023	2.80
39 (a)	2	473	2.69	1.019	2.67
50	1	523	5.86	0.155	14.9
56	1	523	5.29	0.129	14.8
40 (a)	1	523	11.69	0.954	11.95
41 (a)	$\frac{1}{2}$	523	10.13	0.706	12.1
55 (b)	1	523	0.265	0.00
53 (b)	1	523	0.128	0.00
43 (b)	1	523	0.129	0.00

(a) Quantum input increased approximately 11-fold.

(b) Dark reaction.

In Table II are presented the results obtained from experiments in which the quantum input to the cell was varied at constant temperature (200°C.), using dimethyl ether as the reactant. The results show that the ratio $\frac{\text{CH}_4}{\text{C}_2\text{H}_6}$ decreases markedly with increasing intensity but that the ratio $\frac{\text{CH}_4}{(\text{C}_2\text{H}_6)^{1/2}}$ is approximately independent of intensity. These data indicate that the major part of the ethane is formed by the recombination of methyl radicals rather than by a reaction between methyl radicals and dimethylmercury.

TABLE II

EFFECT OF LIGHT INTENSITY ON THE RATES OF FORMATION OF
METHANE AND ETHANE
Dimethyl ether at 200°C.
Duration—2 hr.

Expt. No.	Intensity (relative)	Volume, cc.		$\frac{\text{CH}_4}{\text{C}_2\text{H}_6}$	$\frac{\text{CH}_4}{\text{C}_2\text{H}_6}$
		CH ₄	C ₂ H ₆		
38 39	11	5.4	2.04	2.65	3.78
47	1.8	3.04	0.444	6.9	4.56
49	1.0	1.69	0.345	5.0	2.94
48	0.44	0.53	0.046	11.5	2.46

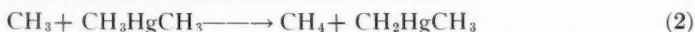
Discussion

Previous investigations have shown that methyl radicals are produced in the photochemical decomposition of dimethylmercury and that those radicals do react with added substances to form methane:—



where R represents a hydrogen atom or an organic free radical.

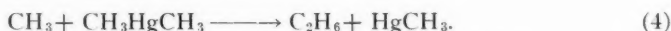
The photolysis of dimethylmercury (6) and the reactions of the methyl radicals produced in that reaction with ethylene oxide (7) and butane (5) were reported after the completion of this investigation. Gomer and Noyes (6) found that methane was produced in the photolysis of dimethylmercury in the absence of any added substance, and concluded that the reaction



occurred with an activation energy of about 9 kcal. mole⁻¹. Actually the Arrhenius line for Gomer and Noyes' results gives a value of about 11 kcal. They also found that, in addition to the recombination reaction:—



methyl radicals disappeared to produce ethane by reaction with dimethylmercury:—



Although Reaction (4) has a very low energy of activation it has a very low steric factor compared with Reaction (3) and therefore contributes only little to the ethane formation.

If all the above reactions are important the kinetics become complicated and, unless the rates of Reactions (2) and (4) are either known or can be ignored compared with those of Reactions (1) and (3), it will be impossible to obtain a value of E_1 . In the present investigation no information was obtained about Reactions (2) and (4) and so it is essential to see whether, under the conditions of our experiments, these rates may be ignored. Reasonably precise information about these reactions may be obtained from previous results and from the data

of the present investigation. Gomer and Noyes (7) concluded that Reaction (4) is much slower than (3) and their results show that, except at very low intensity, the ratio $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^1$ is constant at constant temperature and independent of changes in intensity. Such a result will hold only if most of the ethane is produced by Reaction (3) and an insignificant fraction by Reaction (4). That such a relation is valid in our experiments is shown by the data in Table II and by Fig. 1. Hence Reaction (4) may safely be ignored in our experiments.

It is more difficult to eliminate the effect of Reaction (2) on the rate of formation of methane. However, Gomer and Noyes found that with ethylene oxide the fraction of methane arising from Reaction (1) was a constant fraction of the total and was independent of temperature. Hence we may neglect the correction for Reaction (2) in the case of ethylene oxide, and presumably cyclopropane, in plotting the Arrhenius relation. Also Gomer's results with butane (5) extrapolated to the present condition indicate that 5% to 10% of the total methane in the reactions with methanol and dimethyl ether is formed by Reaction (2). Hence, even if that fraction did vary with temperature the variation will necessitate only a small correction. This treatment appears to be valid because the activation energies of Reaction (1) with ethylene oxide and cyclopropane are almost identical with E_2 and, on the other hand, E_1 for methanol and dimethyl ether are so much smaller than E_2 that the corrections become insignificant.

Since methane and ethane are produced principally by Reactions (1) and (3) respectively, the following relationships are probably valid:—

$$R_{\text{CH}_4} = \frac{d}{dt} [\text{CH}_4] = k_1[\text{CH}_3][\text{RH}]$$

$$R_{\text{C}_2\text{H}_6} = \frac{d}{dt} [\text{C}_2\text{H}_6] = k_3[\text{CH}_3]^2$$

$$R_{\text{CH}_4} = k_2 \frac{R_{\text{C}_2\text{H}_6}^{1/2}}{k_3} [\text{RH}],$$

whence

$$-\frac{E}{RT} = \ln \frac{k_3^{1/2}}{A_1[\text{RH}]} + \ln \frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}^{1/2}} \quad (A)$$

where R_{CH_4} and $R_{\text{C}_2\text{H}_6}$ are the rates of formation of methane and ethane, the k 's are rate constants and A_1 the pre-exponential factor of Reaction (1). If k_3 , A_1 , and RH are temperature independent and constant a plot of $\log \frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}^{1/2}}$

against $\frac{1}{T}$ should give a straight line the slope of which contains E_1 , and the graphs so obtained should be independent of the light intensity. Fig. 1 shows that, with the exception of dimethyl ether at the highest temperature, the above conditions are obeyed reasonably well. In particular it may be noted that with dimethyl ether, increasing the intensity approximately thirtyfold

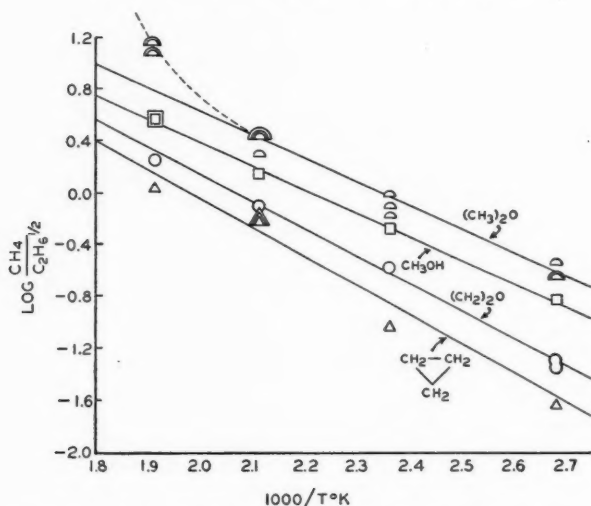
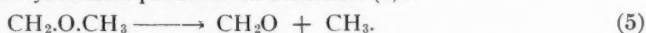


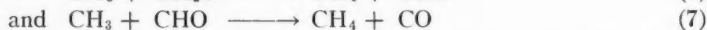
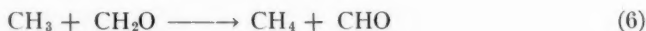
FIG. 1. Arrhenius plot for the reactions of methyl radicals with cyclopropane, ethylene oxide, methanol, and dimethyl ether.

does not significantly affect the values of $\frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}^{1/2}}$ at any temperature at which the reaction was investigated.

With dimethyl ether, the increase in $\log \frac{R_{\text{CH}_4}}{R_{\text{C}_2\text{H}_6}^{1/2}}$ at 250°C. above the value predicted by the kinetic equation is probably caused by the decomposition of the methoxy methyl radical produced in Reaction (1):—



Evidence for Reaction (5) was provided by a study of the effect of temperature on the nature of the products of the mercury photosensitized decomposition of dimethyl ether (8). It has also been shown (13) that hydrogen atoms react rapidly with acetaldehyde at room temperature so that it is likely that the reactions:—



which are rather similar to the corresponding steps in the reaction of hydrogen atoms with acetaldehyde, are also fast. Reactions (5), (6), and (7) are in accord with the increased production of methane and the decreased production of ethane from dimethyl ether at 250°C.

The values for the activation energy of Reaction (1) derived from the slope of the Arrhenius line are given in Table III. Methanol and dimethyl ether are seen to require similar activation energies in reactions of the type of (1), leading

TABLE III
EXPERIMENTAL ENERGIES OF ACTIVATION
AND PRE-EXPONENTIAL FACTORS

Substance	H ₂ *	Cyclopropane	Ethylene oxide	Methanol	Dimethyl ether
E_1 , kcal. mole ⁻¹	9.1	10.2	9.6	8.2	8.0
$\frac{P_1}{P_3^{\frac{1}{2}}} \times 10^4$	6.4	5.2	7.3	3.1	4.8

*Taken from ref. (9)

to the belief that with methanol the hydrogen atom is removed from the methyl rather than from the hydroxyl group. This is in agreement with the results of the mercury photosensitized reactions of methanol (10) in which it was shown that Hg(³P₁) atoms and hydrogen atoms dehydrogenate the methyl group rather than the hydroxyl radical.

The values found for the energies of activation fall into two rather well defined groups—for methanol and dimethyl ether $E_1 \approx 8$ kcal. mole⁻¹ and for cyclopropane and ethylene oxide $E_1 \approx 10$ kcal. mole⁻¹. The first group requires a lower energy than the second although primary C-H bonds are involved in the first group and secondary C-H bonds in the second. Also the value found for the activation energy involving secondary C-H bonds is higher than the values of 5.5 and 8.4 kcal. found by Smith and Taylor (11) and Gomer (5) respectively for the reaction of methyl radicals with *n*-butane, and ascribed by them to the secondary C-H bonds in that compound. It is likely that the high value found for the three membered ring compounds is caused by the strengthening of the C-H bonds in cyclopropane and ethylene oxide, relative to those in a compound such as *n*-butane. This may be connected with the deformation of the C-C bonds of the ring. Recent measurements (1) of the geometry of ethylene oxide show that the H-C-H angles differ significantly from the normal values in the paraffin hydrocarbons. The difference found leads to the belief that the C-H bonds in ethylene oxide, and presumably in cyclopropane, approximate to the sp² type and may therefore be expected to be somewhat stronger than the sp³ hybrid bonds normally found in hydrocarbons. The results also suggest that the primary C-H bonds in methanol and dimethyl ether are somewhat weaker than those in paraffin hydrocarbons. This may be due to the possibility of resonance



in the oxygen containing radicals which will tend to stabilize the radical relative to the ether or alcohol and thus cause some weakening of the C-H bond. There is no possibility of resonance of the above type in the alkyl radicals.

Estimates of the probability factors (P) in the reactions of methyl radicals by Reaction (1) may be obtained from the equation:—

$$\frac{P_1}{P_3^{1/2}} = \frac{Z_3^{1/2}}{Z_1} \cdot \frac{R_1}{R_3^{1/2}} \cdot \frac{e^{E/RT}}{RH},$$

where $E = E_1 - \frac{1}{2}E_3$ and the other symbols have their usual significance. The diameter of methyl radicals was taken as 3×10^{-8} cm. and the other compounds were assumed to have diameters of 5×10^{-8} cm. The values of $\frac{P_1}{P_3^{1/2}}$ are listed in Table III in which is included, for comparison, the value of $\frac{P_1}{P_3^{1/2}}$ previously found (9) for the similar reaction of methyl radicals with hydrogen. With the possible exception of methanol the results show that, for all the compounds investigated and for hydrogen, $\frac{P_1}{P_3^{1/2}}$ is about 6×10^{-4} . Since P_3 cannot be greater than 0.5, the maximum value of P_1 is about 4×10^{-4} . Such a value, which is a maximum, is in sharp contrast to the recent contention (3) that the value of the probability factors in metatheses of the type of (1) are about 10^{-1} and are always greater than 10^{-2} . Actually the results obtained here are not inconsistent with those suggested in an earlier paper (12) from this laboratory.

Acknowledgment

It is a pleasure for us to acknowledge the laboratory assistance given by Mr. Emery Schingh. We wish to record our indebtedness to Dr. E. W. R. Steacie and Mr. A. F. Trotman-Dickenson for many discussions.

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THE PAPILIONACEOUS ALKALOIDS

VII. LUPINUS ARBOREUS SIMS^{1,2}

BY LÉO MARION

Abstract

Lupinus arboreus Sims has been found to contain two main alkaloids, *l*-sparteine and *d*-lupanine together with a small quantity of *l*-lupanine. There may be present a trace of *d*-sparteine, but no other alkaloid could be detected.

The tree lupine, *Lupinus arboreus* Sims, is a shrub growing up to 10 ft. in height, native to California. A quantity of the leaves and twigs obtained from the Dominion Experimental Farm, Ottawa, through the courtesy of Dr. H. A. Senn, was used for the investigation of the alkaloid content of the plant. The main alkaloid found was *l*-sparteine, while the second in importance was *d*-lupanine. The latter was accompanied by a small quantity of *l*-lupanine isolated as the racemic base and identified through its salts and X-ray powder pattern. *d*-Lupanine possesses the same configuration as, and on reduction gives rise to, *l*-sparteine (1). Similarly, *l*-lupanine has the configuration of *d*-sparteine (1, 3). Although there are exceptions reported (5), whenever sparteine and lupanine occur together it is usually the *d*-form of one that accompanies the *l*-form of the other (2, 4). The occurrence of some *l*-lupanine in this plant prompted a search for *d*-sparteine. From the final mother liquor of the crystallization of *l*-sparteine dipicrate, there was isolated a very small quantity of a picrate, the melting point of which was unchanged by admixture with *dl*-sparteine dipicrate. However, owing to paucity of material, this indication of the presence of the *d*-base could not be definitely confirmed.

Experimental

The dried and ground plant (3.7 kgm.) was extracted with methanol in Soxhlets and the combined extract concentrated on the steam bath. Water was added, the mixture acidified to congo red with hydrochloric acid and heated on the steam bath until the remaining methanol had largely evaporated (six hours). After cooling under the tap, the mixture was kept in the refrigerator overnight and filtered with suction. The insoluble material was again heated (three hours) with dilute hydrochloric acid, cooled as before and filtered. The combined filtrates were extracted with several large portions of ether, alkalinized with ammonium hydroxide and extracted exhaustively with chloroform. The chloroform extract was evaporated to dryness on the steam bath and the residual basic material dissolved in 10% hydrochloric acid. The resulting clear solution was washed with several portions of ether, alkalinized with ammonium hydroxide, and extracted with chloroform in a continuous liquid-liquid extractor.

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² For Part VI, see *J. Org. Chem.*, 13: 780. 1948.

Evaporation of the chloroform extract on the steam bath left the crude base as a brown oily gum, wt. 11.8 gm., yield 0.319%. The crude base when distilled *in vacuo* yielded the following fractions: I, b.p. 100–105°C. (0.2 mm.) colorless oil, wt. 0.5146 gm.; II, b.p. 110–135°C. (0.1 mm.) colorless oil, wt. 2.0364 gm.; III, b.p. 135–155°C. (0.1 mm.) colorless oil, wt. 1.4513 gm.; IV, b.p. 155–180°C. (0.1 mm.) brown, thick oil, wt. 0.9258 gm.; V, b.p. 180–240°C. (0.4 mm.), light brown gum, wt. 0.860 gm.; VI, an appreciable undistilled residue.

l-Sparteine

Fraction I was dissolved in methanol and added to a solution of twice its weight of picric acid in methanol. A crystalline picrate separated immediately which was recrystallized from acetone-methanol. It consisted of pale yellow needles, m.p. 208°* either alone or after admixture with an authentic specimen of *l*-sparteine dipicrate. Some of the dipicrate (0.3 gm.) was decomposed by shaking with ether and dilute hydrochloric acid, and the base recovered from the aqueous acid solution was distilled *in vacuo*. The colorless oil, wt. 74.9 mgm., had $[\alpha]_D^{28} - 16.51^\circ$ (*c*, 0.599 in abs. ethanol). The solution used for the determination of the optical rotation was neutralized with 65% perchloric acid, diluted with water, and evaporated until free of ethanol. To the concentrated aqueous solution one drop of ammonium hydroxide was added and the precipitated perchlorate filtered. Recrystallized from methanol-ether, the perchlorate consisted of fine colorless needles, m.p. 172°C., either alone or after admixture with *l*-sparteine monoperchlorate.

Fraction II, on treatment with picric acid yielded a further and larger quantity of *l*-sparteine dipicrate.

The collected mother liquors from the crystallization of *l*-sparteine dipicrate, when concentrated, yielded a further quantity of the salt. From the final mother liquor a small quantity of picrate crystallized which melted at 203°C. either alone or after admixture with *dl*-sparteine dipicrate. However, insufficient material was isolated to permit confirmation of the identity of the racemic base thus indicated.

d-Lupanine

The methanolic liquor from fraction II from which the sparteine dipicrate had crystallized was concentrated until no more picrate separated and then evaporated to dryness. The residual uncrystallizable picrate was decomposed by shaking with dilute (1:1) hydrochloric acid and ether and the base recovered from the acid solution distilled *in vacuo*. It yielded a small quantity of sparteine and a yellowish oil, b.p. 160–180°C. (0.4 mm.). The latter was dissolved in methanol and the solution made just acid to congo red by the dropwise addition of 65% perchloric acid. The cautious addition of ether caused the separation of a crystalline perchlorate which after two recrystallizations from methanol-ether was obtained as colorless, feathery triangular aggregates, m.p. 215°C.,

* All melting points are corrected.

either alone or after admixture with an authentic specimen of *d*-lupanine perchlorate. Calc. for $C_{15}H_{24}ON_2 \cdot HClO_4$: C, 51.65; H, 7.17; N, 8.03%. Found: C, 50.20, 50.12; H, 7.54, 7.58; N, 7.56, 7.54%. The perchlorate, when mixed with *l*-lupanine perchlorate, melted at 244°C. and this mixture on admixture with *dl*-lupanine perchlorate (m.p. 249°) melted at 246°C. Some of the base was recovered from the perchlorate by alkalizing an aqueous solution of the salt with ammonium hydroxide and extracting with chloroform. The base was distilled *in vacuo*; it had $[\alpha]_D^{25} + 61.77^\circ$ ($c = 0.85$ in methanol). The literature records $[\alpha]_D + 61.4^\circ$ in acetone (1). The base (0.2191 gm.) was dissolved in water and ammonium thiocyanate (0.067 gm.) added to the solution which was subsequently evaporated to dryness under reduced pressure. The crystalline residue was dissolved in methanol (2 cc.) and the solution diluted with ether (0.5 cc.). On standing, the thiocyanate crystallized; it was recrystallized once from methanol-ether and again from acetone from which it separated as beautiful light brown prismatic plates, m.p. 185°C. $[\alpha]_D^{20} + 54.66^\circ$ ($c = 1.666$, in water). The literature (1) records $[\alpha]_D + 55.6^\circ$ for *d*-lupanine thiocyanate.

A small quantity of the base was dissolved in methanol and the solution made just acid to congo red by the dropwise addition of methanol containing two drops of concentrated hydrochloric acid. The solution was evaporated to dryness, the residue dissolved in methanol, and the solution again evaporated to dryness. The residue was dissolved in methanol (0.5 cc.) and acetone added to the point of incipient turbidity. After standing in the refrigerator for some time the base hydrochloride crystallized as colorless, short, prismatic needles, which fused at 145–150°C., solidified and melted at 224°C. Calc. for $C_{15}H_{24}ON_2 \cdot 2HCl \cdot 1.5H_2O$: C, 51.72; H, 8.33%. Found: C, 52.21, 52.32; H, 8.49, 8.51%. The molten hydrochloride crystallized on cooling and when heated again melted at 249°. An authentic sample of *d*-lupanine dihydrochloride behaved similarly and finally melted at 263°C. A mixture of the base dihydrochloride and *d*-lupanine dihydrochloride behaved similarly and finally melted at 258°C. It is known that the first melting point of *d*-lupanine dihydrochloride corresponds to the loss of water of crystallization; the second is that of the dihydrochloride and is accompanied by loss of hydrogen chloride, so that the final melting point is that of the monohydrochloride (3). Fractions III and IV also yielded *d*-lupanine.

dl-Lupanine

Fraction V was dissolved in methanol and converted to the perchlorate by the usual method. This perchlorate, after two recrystallizations from boiling methanol, consisted of colorless triangular plates which melted at 118°C. when freshly prepared, but after standing a few days fused slightly at 198°C. and melted at 231°C. In admixture with *d*-lupanine perchlorate (m.p. 215°C.) it melted at 224.5°C. while in admixture with *l*-lupanine perchlorate (m.p. 213°C.) it melted at 234°C. The former mixture in admixture with *dl*-lupanine perchlorate (m.p. 249°C.) melted at 224–235°C. Calc. for $C_{15}H_{24}ON_2 \cdot HClO_4 \cdot CH_4O$: C, 50.46; H, 7.62; N, 7.36%. Found: C, 50.00, 49.96; H, 7.52, 7.44; N, 6.94,

6.98%. The base, therefore, consisted of *dl*-lupanine containing an excess of the *d*-isomer. The identity of the base was further confirmed by a comparison of the X-ray powder pattern of its perchlorate with that of *d*-lupanine perchlorate. These were identical in every respect. In order to ascertain that the identity of the patterns was not due to the predominance of the chlorine atom, the patterns were compared with that of anagryne perchlorate. Although anagryne differed from lupanine only in that it contained a pyridone ring instead of the piperidone ring of the latter, the X-ray powder pattern of its perchlorate was markedly different from that of lupanine perchlorate. The X-ray powder pattern of *l*-sparteine perchlorate was also quite different from either of the other patterns.

The residue left after distillation of the crude bases was dissolved in dilute hydrochloric acid, the solution filtered to remove the insoluble material, alkalinized with ammonia and extracted with chloroform. The extract was evaporated to dryness on the steam bath and the residue fractionated *in vacuo*. Each fraction obtained yielded further small quantities of the bases already described.

Acknowledgment

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THE DEGRADATION OF POLYSTYRENE

I. A STUDY OF THE POLYMERIZATION AND DEPOLYMERIZATION OF POLYSTYRENE¹

BY D. S. MONTGOMERY² AND C. A. WINKLER

Abstract

The steady state obtained by Mesrobian and Tobolsky when toluene solutions, containing the same total weight concentration but varying proportions of styrene and polystyrene, were exposed to ultraviolet light at elevated temperatures was shown to depend upon the catalytic conditions. It was therefore concluded that this state does not represent a true thermal equilibrium between monomer and polymer. In the absence of monomer, polystyrene in toluene solution underwent chain scission on irradiation with ultraviolet light or treatment with benzoyl peroxide and air, even when the average chain length was less than that corresponding to the steady state. When monomer and polymer coexist in the presence of light or large quantities of oxidizing agents, a steady state arising from the polymerization of styrene and the simultaneous degradation of polystyrene appeared to be a transient phenomenon. Ultimately the monomer polymerizes and degradation becomes the dominant reaction. The experimental results indicated that a given mass of benzoyl peroxide or air brought about the scission of a definite number of linkages, resulting in a definite decrease in the relative viscosity. In the absence of oxidizing agents or light, polystyrene in toluene solution was remarkably stable at 100°C.

Introduction

Previous studies in this laboratory (2) have shown that the addition of potassium persulphate to a monomer-free latex of butadiene-styrene copolymer can induce a cross-linking reaction, the rate of which is proportional to the persulphate ion concentration. Since the polymer chains in this reaction were unsaturated, it was a point of interest to determine whether a cross-linking reaction might also be made to occur between saturated polymer molecules, such as polystyrene, in the presence of a suitable catalyst and solvent.

In the absence of solvent, Baker (1) was able to bring about the cross-linking of pure polyundecanoates, which contain no unsaturated bonds or monomers of functionality greater than two (5) but do possess α -methylene hydrogen which has long been recognized as reactive (9).

There is also experimental evidence that chain branching may result from free radical attack upon saturated chains (10). This behavior is in keeping with suggestions made by Flory (7) and Taylor and Tobolsky (17) that branched vinyl polymer could result from chain transfer reactions involving polymer molecules. Further experimental evidence in support of this view was obtained by Carlin and Shakespeare (4) who showed that the thermal polymerization of *p*-chlorostyrene in the presence of polymethacrylate produced molecules which contained both types of structural units.

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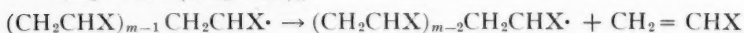
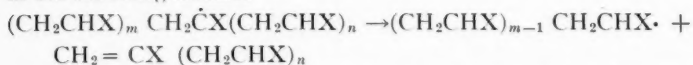
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.

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In view of this it was thought that the addition of a catalyst to a system containing saturated polymer, but no monomer, might result in an increase in the molecular weight by reason of such cross-linking and branching reactions. The use of viscosimetric measurements to detect the presence of cross-linking was suggested by the work of Staudinger and Husemann (16) who showed that this technique was capable of detecting the influence of one mole of divinyl benzene in the presence of 30,000 moles of styrene after polymerization.

While branching and cross-linking of polystyrene may occur under conditions similar to those employed by Mesrobian and Tobolsky, depolymerization may be the dominant reaction. It was first suggested by Chalmers (6) that this process occurred by a chain reaction of an inverse character to that involved in the formation of the polymer. More recently, Taylor and Tobolsky (17) have postulated that the first step in the process of degradation probably involves the removal of a hydrogen atom of the polymer chain. This may presumably occur by thermal action (14), but, at room temperature, it seems more probable that the majority of these active centers are formed by the action of oxygen or free radicals upon the polymer chain (12).

By analogy with the mechanism for the self-disproportionation of hydrocarbon radicals, suggested by Rice and Rice (14) the depolymerization of vinyl polymers, following the initial attack of oxygen, may be visualized as occurring in the following manner



Taylor and Tobolsky (17) have estimated the activation energy of the degradation reaction to be of the order of 25 kcal. per mole, suggesting that fairly rapid depolymerization might be obtained at moderate temperatures. Assuming that depolymerization occurs through the same intermediate free radicals as polymerization, Blatz and Tobolsky (3) and Flory (8) predicted on thermodynamical and statistical mechanical grounds that a most stable distribution of chain length should exist consistent with environmental conditions.

Mesrobian and Tobolsky (11) have shown experimentally that the viscosities of toluene solutions containing the same total weight concentration of styrene and polystyrenes of various chain lengths all converged to a fixed value during exposure of the solutions to ultraviolet light at 100°C. This was interpreted as showing that the degradation and polymerization processes are intimately related, and that a steady state, possibly representing a thermal equilibrium, may be reached at which the rate of polymerization is equal to the rate of depolymerization. Similar results were obtained by Spodheim, Badgley, and Mesrobian (15) when the experiments were made in the absence of light but in the presence of benzoyl peroxide.

The available information suggested to the present authors that it might be possible to polymerize further a polystyrene of molecular weight less than that

corresponding to the steady state, and to study the kinetics of this reaction in the presence of free radical catalysts. Failure to observe polymerization led to a more detailed investigation of the behavior of such systems. The results are reported in the present paper and in two that follow.

Experimental

Materials

Styrene was supplied by the Polymer Corporation, Sarnia. It was washed several times with *N*/10 sodium hydroxide to remove the *t*-butylcatechol present as polymerization inhibitor. It was then washed with water, dried over calcium chloride, and distilled three times under reduced pressure.

Eastman Kodak reagent grade benzoyl peroxide was used without further purification.

Merck reagent grade toluene was dried over calcium chloride and distilled before using.

Polyisobutylene was supplied by the Polymer Corporation.

Apparatus

The reversible viscosimeters were of the same design as those used by Mesrobian and Tobolsky (11).

The thermostats for the experiments performed in darkness were oil baths in which temperatures were maintained to within 0.5°C.

For the photochemical experiments an air oven was used in which the temperature was maintained at $100 \pm 2^\circ\text{C}$., and the air circulated to eliminate temperature gradients. The viscosimeters were suspended directly over a circular opening through which the light source, a G.E., type RS (275-W.), Sunlamp was directed, at a distance of two inches from the viscosimeters.

Simultaneous Polymerization of Styrene and Degradation of Polystyrene

A series of experiments was first undertaken, both in the presence and the absence of light, in an effort to locate the steady state described by Mesrobian and Tobolsky.

Twelve viscosimeters were each charged with 1.600 ± 0.003 gm. of a solution containing 0.125 gm. benzoyl peroxide in 99.88 gm. styrene, and sealed off in air. The viscosimeters were placed in a thermostat at 100°C . and removed in pairs after various periods of time ranging from 20 min. to nine hours. They were then opened, 10 cc. of toluene added to each, and resealed in air. Two viscosimeters, henceforth referred to as the zero hour sample, were prepared in the same way, but not subjected to the bulk phase polymerization. The relative viscosities of the 12 solutions were determined at 25°C . The sealed viscosimeters were then returned to the thermostat at 100°C . and removed periodically to follow the change in viscosity.

In Fig. 1, the results, shown by the solid lines, are contrasted with those reported by Mesrobian and Tobolsky (11). For the purpose of graphical representation, the results of duplicate determinations, which generally agreed to within 0.5%, were averaged. In these experiments, performed in the absence of light, a steady state of the type found by Mesrobian and Tobolsky was not evident in less than 5000 hr. There was an indication, however, that a certain mixture of polymer and monomer exists, such that, on dilution with toluene, no change in viscosity of the solution occurs at 100°C. For convenience this will be referred to as the visco-static state. From Fig. 1 it is apparent that the relative viscosity corresponding to this state in the absence of light is of the order of 90 as compared with a value of 7 found by Mesrobian and Tobolsky in the presence of light (11).

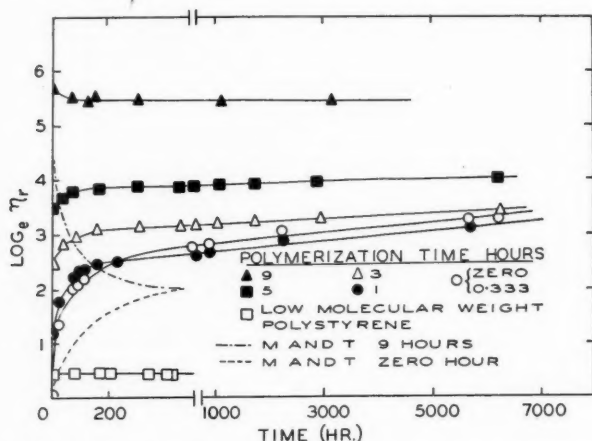


FIG. 1. The polymerization and degradation of mixtures of styrene and polystyrene in toluene solution in the absence of light. Temp., 100°C.

It can be seen from Fig. 1 that the nine hour sample underwent slow degradation following the addition of toluene and air, a limiting value of the viscosity being reached after about 100 hr. This degradation may be attributed largely to attack by oxygen of the air sealed into the viscosimeters, since it is likely that the benzoyl peroxide had been largely consumed during the initial nine hour polymerization (13). This oxygen was apparently used up during the first 100 hr., and the fact that the viscosity subsequently remained constant for 3000 hr., gives an indication of the stability of polystyrene in the absence of oxidizing agents.

Since the viscosity corresponding to the visco-static state in the absence of light disagreed markedly with the results reported by Mesrobian and Tobolsky (11), experiments were undertaken to study the behavior of solutions of styrene and polystyrene, in the presence of light.

Styrene was polymerized in viscosimeters and subsequently diluted with toluene, as previously described. Instead of preparing zero hour samples, two viscosimeters were heated at 100°C. for five minutes in conformity with the procedure of Mesrobian and Tobolsky (11). After dilution the viscosimeters were placed in the air oven at 100°C. where they were exposed to ultraviolet light. The change of viscosity with time was determined, and is shown in Fig. 2.

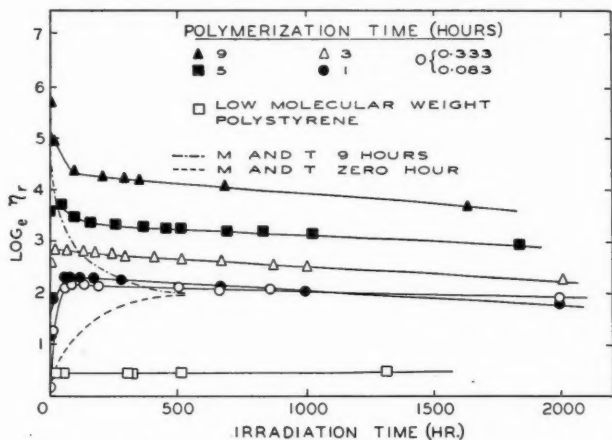


FIG. 2. The polymerization and degradation of mixtures of styrene and polystyrene in toluene solution in the presence of light. Temp., 100°C.

The viscosities of the various samples did appear to converge to some extent, but the convergence to a single value was not as clearly marked as indicated by the work of Mesrobian and Tobolsky (11). It can be seen that the viscosities of the five minute samples first increased above the steady state value and then steadily declined to a value below it. A similar effect has been obtained by Spodheim, Badgley, and Mesrobian (15).

Attempt to Induce Polymerization, Cross Linking, or Branching of Polystyrene

A further experiment was made to reveal whether a polystyrene of low molecular weight could be polymerized further in the absence of monomer. The polystyrene was prepared by allowing mixtures of the following composition to polymerize at 140°C. for two hours in sealed Pyrex tubes containing 10 cc. of air.

20 cc. toluene
1 gm. benzoyl peroxide
2 cc. styrene.

The resulting polymer was precipitated with methanol. The coacervate was washed thoroughly with methanol to remove the decomposition products of benzoyl peroxide, and dried for three days in a vacuum oven at 80°C. A 1.6 gm. sample of the polymer was dissolved in 10 cc. of toluene, and the solution

placed in a reversible viscosimeter which was then sealed off in air. The viscosimeter was placed in a thermostat at 100°C. and the change of viscosity with time determined.

From Fig. 1 it can be seen that the $\log_e \eta_r$ appears to remain constant. Actually the relative viscosity η_r decreased very slightly, from 1.64 to 1.61. When the experiment was repeated exposing the viscosimeter to ultraviolet light at 100°C. instead of heating it in an oil bath at the same temperature, the results were similar. After 1312 hr. exposure, the relative viscosity decreased from 1.62 to 1.59 as shown in Fig. 2. A similar experiment was made in which successive increments of benzoyl peroxide and air were added to the solution at 100°C. in the absence of light. The relative viscosity remained essentially constant at 1.63, over a period of 950 hr., during the last 500 of which, 18 successive increments of benzoyl peroxide ranging from 0.005 to 0.01 were added.

There was therefore no evidence of cross-linking, branching, or reversible polymerization under these conditions, even after relatively large additions of benzoyl peroxide. The solution appeared to be entirely clear, though yellow in color. In the absence of branching or gel formation, it becomes possible to degrade a high molecular weight polystyrene and follow the number of linkages broken as a function of the benzoyl peroxide and air added.

The polystyrene used in the following experiments was prepared by heating a solution of the composition given below for two hours in a sealed Pyrex tube containing 15 cc. of air.

6.61 cc. styrene
37.5 cc. toluene
0.0075 gm. benzoyl peroxide.

The tube was allowed to stand overnight at room temperature. It was then opened and the contents poured into an equal volume of methanol. The coacervate was washed with methanol and dried to constant weight in a vacuum oven at 76°C. A solution of 1.6 gm. of this polymer in 10 cc. of toluene was placed in a reversible viscosimeter and its viscosity determined, after which 0.002 gm. of benzoyl peroxide was added, the viscosimeter sealed in air, and the change of viscosity with time at 100°C. determined. The results are shown in Fig. 3.

Following an initial decrease during the first 100 hr., the viscosity remained constant during the following 1200 hr. It is apparent that the initial presence of styrene together with the polymer is not a necessary requirement for stability. On reopening the viscosimeter and recharging it with 0.002 gm. benzoyl peroxide, a further decrease in viscosity occurred but this time significantly smaller than that following the first addition. This behavior characterized further successive additions of benzoyl peroxide. A possible explanation for the apparent decrease in the efficiency of benzoyl peroxide in bringing about a decrease in the relative viscosity is that the reaction is inhibited by the presence of the decomposition products from previous additions. However, it

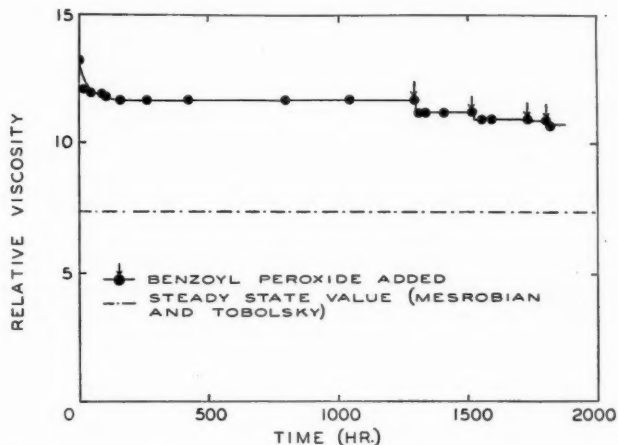


FIG. 3. The degradation of polystyrene in toluene solution by benzoyl peroxide and air. Temp., 100°C.

seems more probable that the effect is to be attributed to the relation between the viscosity and the number average molecular weight of the polymer. As degradation continues it becomes necessary to sever a greatly increased number of chains to cause the same decrease in viscosity.

To determine how other linear polymers would behave, this experiment was repeated using polyisobutylene instead of polystyrene. A reversible viscosimeter was charged with 10 cc. of a solution containing 4 gm. polyisobutylene in 100 cc. of toluene. The change of viscosity following successive additions of benzoyl peroxide was determined. The results described in Fig. 4 are essentially similar to those obtained with polystyrene, a point being reached where the

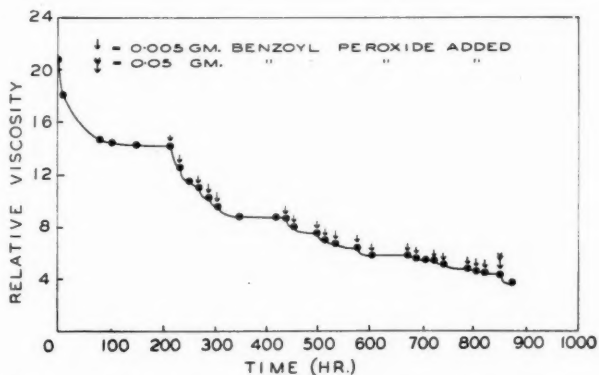


FIG. 4. The degradation of polyisobutylene in toluene solution by benzoyl peroxide and air. Temp., 100°C.

addition of 0.005 gm. benzoyl peroxide and air caused virtually no further decrease in viscosity. However, on increasing the amount of benzoyl peroxide added to 0.05 gm., the viscosity again decreased significantly. This is in keeping with the suggestion previously made that as the polymer chains become shorter, a greatly increased number of bonds must be ruptured to obtain the same decrease in viscosity. This in turn requires the addition of larger quantities of scission agent.

Discussion

The apparent steady state at 100°C. approached by various mixtures of styrene and polystyrene dissolved in toluene was found to depend upon the catalytic conditions, such as the presence of oxidizing agents and the action of light. In the absence of these catalysts polystyrene was very stable at 100°C. It would therefore appear that a thermal equilibrium between monomer and polymer, the position of which would be independent of the catalytic conditions, does not exist in these systems.

Styrene polymerizes in toluene solution in the absence of benzoyl peroxide and light at 100°C. to give a relatively high molecular weight polymer. These molecular weights cannot be approached by irradiation or addition of catalyst to low molecular weight polystyrene at the same concentration and temperature.

In the absence of monomer, polystyrene failed to undergo polymerization even when the molecular weight was much less than that corresponding to the steady state described by Mesrobian and Tobolsky (11). Instead, a slight degradation was always observed.

On the assumption that the behavior of polystyrene in the presence of free radicals in toluene solution was not altered by the presence of monomer, the preceding experiments demonstrate that the apparent steady state arising from the simultaneous degradation of polystyrene and polymerization of styrene was a transient phenomenon. Ultimately the monomer polymerizes, and degradation becomes the dominant reaction. This was in accord with the experimental observation that the viscosity of toluene solutions of styrene undergoes an initial increase. Then, after reaching a maximum, the viscosity steadily declines on prolonged irradiation or extensive attack by oxygen and benzoyl peroxide. As previously mentioned, this effect also appears to have been obtained by Spodheim, Badgley, and Mesrobian (15).

The observation, that neither extensive irradiation of low molecular weight polystyrene in toluene solution nor the repeated addition of benzoyl peroxide and air caused an increase in viscosity or visible sign of gel formation, led to the conclusion that cross-linking and branching of polystyrene under these conditions was not pronounced. This suggested the possibility of studying the degradation of high molecular weight polystyrene without the interpretation of the viscosity measurements being obscured by simultaneous branching and cross-linking reactions.

In the absence of light the addition of a given mass of benzoyl peroxide and air to a 16% solution of polystyrene in toluene at 100°C. did not cause a continued decrease in viscosity. After 100 hr. the viscosity would remain constant indefinitely. This suggested that a given mass of benzoyl peroxide was responsible for the scission of a definite number of linkages. This qualitative information formed the background for the more detailed study of the degradation of polystyrene presented in the succeeding papers.

Acknowledgment

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THE DEGRADATION OF POLYSTYRENE

II. THE SYNTHESIS AND DEGRADATION OF POLYSTYRENE POSSESSING THE KUHN-SCHULZ CHAIN LENGTH DISTRIBUTION¹

BY D. S. MONTGOMERY² AND C. A. WINKLER

Abstract

By polymerizing styrene in emulsion it was possible to synthesize polystyrenes of known number average molecular weight, the chain length distributions of which corresponded closely to the Kuhn-Schulz relation $N_p = N_0 p^{p-1} (1-p)^2$. This enabled a relation between intrinsic viscosity and number average molecular weight to be established for polystyrenes with chain length distributions of this functional form. Assuming this form of chain length distribution to remain unaltered on degradation, it was possible to estimate the average number of scission points per structural unit from viscosimetric measurements. The extent of thermal scission of polystyrene after one week at 144°C. was shown to be negligible, while benzoyl peroxide caused appreciable chain scission at 80°C. and 100°C. The number of scission points estimated from viscosimetric measurements was directly proportional to the mass of benzoyl peroxide added to the system, and the scission appeared to be essentially random over the limited range investigated.

Introduction

The two original suggestions by Mesrobian and Tobolsky (17) that there existed a steady state for which the rates of polymerization and depolymerization of polystyrene were equal, and that there was a possibility of a thermal equilibrium between monomer and polymer, did not appear to be capable of explaining the results obtained in the previous paper (18). On the other hand, it was not easy to account for the convergence of the viscosities of toluene solutions containing the same total weight concentration but various proportions of styrene and polystyrene (17). The observations that neither extensive irradiation nor the addition of catalysts to polystyrene caused gelation under these conditions, and that a given mass of benzoyl peroxide and air appeared to be responsible for a definite amount of scission, suggested that a viscosimetric study of the degradation of polystyrene might clarify this problem (18).

To study quantitatively the scission of linear chain molecules it was necessary to have a method of determining the number of molecular fragments, i.e., the number average molecular weight of the polymer. In addition, it was desired to ascertain whether or not scission of bonds in the polymer chain by free radicals is approximately random.

Montroll (19) and Tuckett (24) have shown that if random breaking of bonds occurs between successive structural units, the distribution of chain

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length on extensive degradation becomes independent of the initial distribution, and that the functional form of the distribution ultimately becomes

$$N_y = N_0 p^{y-1} (1 - p)^2, \quad (1)$$

where N_y represents the total number of chain molecules in the system possessing y structural units, N_0 the total number of structural units in the system, and p denotes the probability that a given bond between two structural units remains intact. This distribution function is precisely that derived by Kuhn (15) and Klages (9) for the degradation of a linear polymer of infinite length, and that derived by Schulz (22) for the distribution of chain length arising from polymerization of vinyl monomers, and will subsequently be referred to as the Kuhn-Schulz distribution.

It followed from the work of Montroll and Tuckett that if the polymer initially possessed the Kuhn-Schulz distribution of chain length, the functional form of this distribution would remain unaltered during random scission of the linkages between successive structural units. Evidently, it was desirable to establish the dependence of the intrinsic viscosity $[\eta]$ upon the number average molecular weight M_n for polystyrene possessing this distribution of chain length. Such a relation permits the number average molecular weight or the average number of scission points per structural unit to be estimated, during random degradation, from the measurements of the intrinsic viscosity. If the initial molecular weight of the polymer is large and if the degradation is not too extensive, this relation should remain approximately valid even if the structural units themselves are occasionally severed.

The average number of scission points per structural unit \bar{s} may readily be derived from the number average molecular weight in view of the definition of this quantity. If m_0 is the molecular weight of a structural unit and \bar{y}_n is the number average chain length, \bar{M}_n , the number average molecular weight, is given by the following relation:

$$\bar{M}_n = \bar{y}_n m_0 = \frac{\text{Total number of structural units} \times m_0}{\text{Total number of polymer molecules}} \quad (2)$$

By definition, the total number of scission points s in a system of N_0 structural units is one less than the number of chain molecules, and the following expressions may be derived from Equation (2).

$$\begin{aligned} \bar{M}_n &= \bar{y}_n m_0 = \frac{N_0}{s + 1} m_0, \\ \frac{1}{\bar{y}_n} &= \frac{m_0}{\bar{M}_n} = \frac{s + 1}{N_0} \doteq \frac{s}{N_0} = \bar{s}. \end{aligned} \quad (3)$$

Frequent reference will be made to the quantities $\frac{1}{\bar{y}_n}$ or \bar{s} which from the preceding argument are merely the average number of scission points per structural unit.

Kolthoff (14) established that vinyl polymers of different average chain lengths may be prepared in emulsion by varying the ratio of the monomer to chain transfer agent. It remained to be determined under what conditions polystyrene so prepared would also possess the Kuhn-Schulz distribution of chain length, and to evaluate if possible the ratio of the viscosity average to the number average molecular weight.

Estimation of the Viscosity Heterogeneity Index of Polystyrene Prepared in Emulsion

In the polymerization of polystyrene in emulsion, using fatty acid soaps as emulsifying agents and potassium persulphate as catalyst, it has been shown that small amounts of mercaptans in the recipe do not influence the rate of polymerization at 50°C. The mercaptan acts only as a chain transfer agent or modifier (10, 12). This permits the preparation of polystyrenes of various average molecular weights. At the same time it provides a means for estimating the number average molecular weight, since it has been observed that approximately one mercaptan molecule is combined with each polymer chain (23, 26). The residual mercaptan may be determined by the method of Kolthoff (13), and with the knowledge of the initial mercaptan concentration in the latex the number average molecular weight may be readily evaluated. An approximate estimate of the heterogeneity index or the ratio of the viscosity average to the number average molecular weight may be made from the relative rates of disappearance of the mercaptan and of polymer formation in the following manner.

Schulz (22) demonstrated that if the ratio of the rates of chain propagation and termination remain constant, the distribution of molecular chain length is given by Equation (1). Grinell and Simha (7) have emphasized that this implies a negligible rate of initiation in comparison with the rates of both growth and termination. In the preparation of polystyrene in the presence of a transfer agent, a constant probability p for a growing molecule to add an additional structural unit implies that the ratio of the concentration of monomer to that of the transfer agent is constant, a condition that is rather difficult to achieve experimentally. However, the following approximate calculation, together with the measured values of the regulating index, indicate that if the conversion of monomer to polymer is not permitted to exceed 50%, the distribution of chain length is given to a first approximation by the Kuhn-Schulz relation.

When a basal mole or Avogadro's number, A , of structural units polymerizes in the presence of a definite number of moles of modifier R_0 , for time t , and the fraction f of monomer units is converted to polymer, the total number of structural units composing the polymer is then Af . In the course of polymerization R_c moles of mercaptan combine with polystyrene, leaving R residual moles of modifier. Under the conditions of the experiment where R_0 moles of mercaptan were initially added to the system

$$\begin{aligned} R_0 &= R + R_c \\ \text{and } -dR &= dR_c. \end{aligned} \tag{4}$$

The chemical equation describing the propagation and termination reactions respectively may be written as follows,



The number of molecules of length $X_{n+1} X^\cdot$ formed in an element of time dt is then given by

$$d[X_{n+1} X^\cdot] = K_p [X_n X^\cdot] [X] dt,$$

where K_p is the rate constant of the propagation step.

Similarly the number of growing chains which are terminated in the same element of time is given by

$$d[X_{n+1} R] = K_t [X_n X^\cdot] [R] dt.$$

The probability of a chain X_n unit in length adding an additional monomer unit in time t is therefore

$$\begin{aligned} p &= \frac{K_p [X_n X^\cdot] [X] dt}{K_p [X_n X^\cdot] [X] dt + K_t [X_n X^\cdot] [R] dt} \\ &= \frac{K_p [X]}{K_p [X] + K_t [R]}, \\ \text{whence } \frac{1-p}{p} &= \frac{K_t [R]}{K_p [X]}. \end{aligned} \quad (5)$$

The number of monomer units which have been added to the growing chains having lengths from X_1 to X_n in the element of time dt is

$$A.df = K_p [X] dt \sum_{n=1}^{\infty} X_n X^\cdot. \quad (6)$$

Similarly

$$A.dR_c = K_t [R] dt \sum_{n=1}^{\infty} X_n X^\cdot. \quad (7)$$

From Equations (6) and (7) it follows that

$$\frac{dR_c}{df} = \frac{K_t [R]}{K_p [X]}. \quad (8)$$

By the comparison of Equations (4), (5), and (8), it follows that

$$\frac{1-p}{p} = - \frac{dR}{df}. \quad (9)$$

It has been established experimentally that the rate of modifier disappearance is first order with respect to the conversion of monomer to polymer up to at least 50% conversion (3, 20, 16). That is

$$- \frac{dR}{df} = rR. \quad (10)$$

The quantity r is a constant usually referred to as the regulating index (3). Combining Equations (9) and (10),

$$\frac{1-p}{p} = -\frac{dR}{df} = rR. \quad (11)$$

On integration Equation (10) becomes

$$R_1 = R_0 e^{-rf}, \quad (12)$$

where R_0 and R_1 are respectively the initial and final residual modifier concentrations at conversion f . The number average chain length \bar{y}_n at any conversion f may be readily determined by extending the definition of this quantity given by Equation (2).

$$\begin{aligned} \bar{y}_{nf} &= \frac{\text{The number of structural units in polymer}}{\text{The number of molecules of modifier consumed}} \\ &= \frac{f}{R_0(1 - e^{-rf})}. \end{aligned} \quad (13)$$

The viscosity average molecular weight may be estimated approximately at any conversion within the range of conversion for which r may be regarded as constant by considering an increment of conversion df during which the instantaneous probability of chain propagation has the value p . The number of structural units involved in polymer is $A \cdot df$ and the number of y -mers formed is therefore:

$$p^{y-1}(1-p)^2 A \cdot df. \quad (14)$$

The total number of polymer molecules possessing y structural units at any conversion f may be estimated by summing the number of y -mers in each element of conversion df .

$$N_y = \int_0^f p^{y-1}(1-p)^2 A \cdot df. \quad (15)$$

The viscosity average molecular weight \bar{M}_v and the viscosity average chain length \bar{y}_v may be expressed in the following form:

$$\frac{\bar{M}_v}{m_0} = \bar{y}_v = \left[\frac{\sum_{y=1}^{\infty} N_y \cdot y^{a+1}}{\sum_{y=1}^{\infty} N_y \cdot y} \right]^{1/a}. \quad (16)$$

The value of the sum in the denominator of Equation (16) is the total number of structural units contained in the polymer at conversion f and is equal to Af . In the numerator the summation with respect to y may be approximately replaced by the corresponding integral.

$$\frac{\bar{M}_v}{m_0} = \bar{y}_v = \left[\frac{\int_0^{\infty} \int_0^f y^{a+1} p^{y-1}(1-p)^2 A df dy}{Af} \right]^{1/a}.$$

On interchanging the order of integration and integrating first with respect to y the numerator becomes

$$\left\{ \int_0^f \frac{(1-p)^2}{p} \left[\frac{\Gamma(a+2)}{(-\log_e p)^{a+2}} \right] A df \right\}^{1/a},$$

by making the approximation that $-\log_e p = \frac{1-p}{p}$,

$$(\bar{y}_v)^a = \frac{\Gamma(a+2)}{f} \int_0^f \frac{p^{a+1}}{(1-p)^a} df.$$

The variables p and f may be expressed in terms of R with the aid of Equation (11),

$$(y_v)^a = - \frac{\Gamma(a+2)}{f} \int_{R_0}^{R_1} \frac{1}{(rR)^{a+1}} \cdot \frac{1}{(1+rR)} dR.$$

If $\frac{1}{1+rR}$ is expanded in a power series assuming that the ratio of termination to propagation rR is less than unity the following expression is obtained

$$(y_v)^a = - \frac{\Gamma(a+2)}{f} \int_{R_0}^{R_1} \frac{1}{(rR)^{a+1}} - \frac{1}{(rR)^a} + \frac{1}{(rR)^{a-1}} - \frac{1}{(rR)^{a-2}} \dots dR.$$

Employing the first two terms of the power series and integrating

$$(y_v)^a = \frac{\Gamma(a+2)}{fr^a R_0} \left\{ \frac{1}{ar} \left(\frac{1}{e^{-raf}} - 1 \right) + \frac{R_0}{1-a} \left(\frac{1}{e^{-rf(a-1)}} - 1 \right) \right\}$$

and finally

$$\frac{y_v}{y_n} = \frac{\left[\frac{\Gamma(a+2)}{fr^a} \left\{ \frac{1}{ar} \left(\frac{1}{e^{-raf}} - 1 \right) + \frac{R_0}{1-a} \left(\frac{1}{e^{-rf(a-1)}} - 1 \right) \right\} \right]^{1/a}}{\frac{f}{1 - e^{-rf}}} \quad (17)$$

The fraction f of monomer converted to polymer during the time t , and the initial number of moles of tertiary dodecyl mercaptan per mole of styrene R_0 , were both readily determined. The evaluation of the regulating index r will be described later at greater length. The constant a has as its origin Mark's equation,

$$[\eta] = KM^a,$$

relating the intrinsic viscosity to the molecular weight of a homogeneous polymer. This constant is known to be a function of the molecular weight (1, 8), and experimental values in toluene have been reported for polystyrene between 0.62 and 1.12 (6). For this solvent it seemed preferable to employ a value for a of 0.78 for the series of polymers prepared in emulsion with number average molecular weights ranging from 25,000 to 200,000. This value of a agrees with the value of 0.783 found by Ewart, Tigney, and Wales (4) for unfractionated polystyrene in benzene solution with number average molecular weights in the range 50,000 to 800,000.

On the basis of Mark's equation, Flory (5) has shown the intrinsic viscosity to be related to the viscosity average molecular weight by the following expression:

$$[\eta] = K(\bar{M}_v)^a \quad (18)$$

The ratio $\frac{\bar{M}_v}{\bar{M}_n}$ or viscosity heterogeneity index h of the polystyrenes prepared in emulsion was almost constant over the number average molecular weight range from 25,000 to 200,000. On writing Equation (18) in logarithmic form,

$$\log [\eta] = \log K + a \log h + a \log \bar{M}_n,$$

it may readily be seen that the constancy of h implies a linear relation between $\log [\eta]$ and $\log \bar{M}_n$ with slope a . The value of a derived from the slope of Curve 1 in Fig. 2 was 0.77. The mean between this value and that quoted by Ewart was 0.78, which again suggested the use of this value for a .

Rehner (21) has shown that for polymers possessing the Kuhn-Schulz distribution

$$h = \frac{\bar{M}_v}{\bar{M}_n} \div (\Gamma(a+2))^{1/a}$$

when $a = 0.78$, $h \div 1.90$.

When the measured values of f , R_0 , and r were inserted in Equation (17) and the value of 0.78 used for a , the calculated values of the viscosity heterogeneity index of the polystyrene prepared in emulsion did not differ widely from that corresponding to the Kuhn-Schulz distribution of chain length.

Experimental

PREPARATION OF POLYSTYRENE WITH THE KUHN-SCHULZ DISTRIBUTION OF CHAIN LENGTH

The procedure followed was essentially that described by Kolthoff and Harris (12).

Apparatus

Polymerization vessels.—Four-ounce bottles with a metal screw cap and a Neoprene gasket were used. The total weight of the latex charge per bottle was 95 gm., so that a space of approximately 20 cc. remained in the bottle.

Thermostat.—The polymerizations were performed in a water bath maintained at $50^\circ \pm 0.1^\circ\text{C}$. The bottles were rotated end over end at a rate of 35 r.p.m. in a circle of 10 in. diameter.

Materials

Styrene was distilled once under reduced pressure to free it from the inhibitor.

The soap used was Rubber Reserve Corporation silica free flakes. Sharples tertiary dodecyl mercaptan was employed as the modifier.

Procedure

The recipe on the basis of 100 parts by weight of monomer was as follows:

- 100 parts styrene monomer,
- 180 " water,
- 5 " soap,
- 0.3 " $K_2S_2O_8$,
- 0.5 to 0.0625 parts tertiary dodecyl mercaptan.

Each 4-oz. bottle was charged with one third of the above recipe in the following manner. Fifty cubic centimeters at 50°C. of 3.36% soap solution was introduced into each bottle. The caps were screwed down and the bottles cooled. They were subsequently reopened and charged with 33.3 gm. styrene in which sufficient tertiary dodecyl mercaptan was dissolved to yield a polymer of the desired molecular weight. To this was added 12.26 gm. of a 0.896% solution of $K_2S_2O_8$ in water. The bottle was immediately swept with nitrogen and the cap once again screwed on. The bottles were rotated in the thermostat for three minutes, then withdrawn and given a vigorous manual shaking to break all the solid soap at the bottom of the bottles and to emulsify the styrene thoroughly. The bottles were then returned to the thermostat for 57 min. This time was maintained constant so that the fractional conversion of monomer to polymer would be the same in each bottle whether it contained a large or small amount of modifier. At the conclusion of this period the bottles were removed and sampled for the determination of residual mercaptan.

Determination of the Residual Mercaptan

A 5 cc. sample of latex was added to 100 cc. of absolute ethanol and vigorously stirred. The remaining persulphate ion was reduced by adding 2 cc. of 0.01 *M* ferrous ion solution in 0.05 *M* sulphuric acid. The alcoholic solution was permitted to stand for five minutes, then 2 cc. of concentrated ammonia was added. The resulting solution was titrated amperometrically with standard silver nitrate solution, using a rotating electrode of the design described by Kolthoff and Harris (11).

Determination of the Yield of Polymer

The yield of polystyrene per 4-oz. bottle was determined by slowly pouring the contents of the bottle into 500 cc. of butanol, which was vigorously stirred. The solution was then filtered, the polystyrene washed several times with water and dried in a vacuum oven overnight. The yield of polymer, or per cent conversion, was estimated by weighing the dried polymer and making allowance for the aliquot samples removed for mercaptan analysis.

Determination of the Intrinsic Viscosity of Polystyrene Prepared in Emulsion

The intrinsic viscosity of the unfractionated polymer from each 4-oz. bottle was determined to establish the relation between the viscosity average and the

number average molecular weight. Two viscosimeters of the Ubbelohde type (25) were employed with a glass bulb at the base of the viscosimeter sufficiently large to permit successive dilutions to be made in the viscosimeter. The kinetic energy correction was considered to be negligible since the toluene drainage times of the 3 cc. measuring bulbs were 131 and 164 sec. respectively. Both viscosimeters yielded identical values of the relative viscosity of polymer solutions of different concentrations over a wide range of molecular weight.

A known weight of polymer was introduced into the viscosimeter, solvent was added from a calibrated pipette, and the specific viscosity of the solution determined. The intrinsic viscosity $[\eta]$ was then obtained by extrapolation of $\frac{\eta_{sp}}{c}$ to zero concentration.

Determination of the Regulating Index

The regulating index r is defined as

$$r = \frac{-d \log_e R}{df} = -2.303 d \frac{\log_{10} R}{df},$$

where f = the fractional conversion of monomer to polymer at any time t ,

R = moles of residual mercaptan per mole of monomer at time t .

The value of r was obtained by plotting $\log_{10} R$ against the per cent of conversion f as shown in Fig. 1. The slope of this curve was almost constant between zero and 60% conversion. The value of r determined from this slope was found to be equal to 2.02.

The residual mercaptan and per cent of conversion were evaluated by polymerizing styrene in emulsion, employing the previous recipe and under the same conditions with the following modifications. The initial concentration of tertiary dodecyl mercaptan was 0.118 gm. per 100 gm. styrene. The size of the

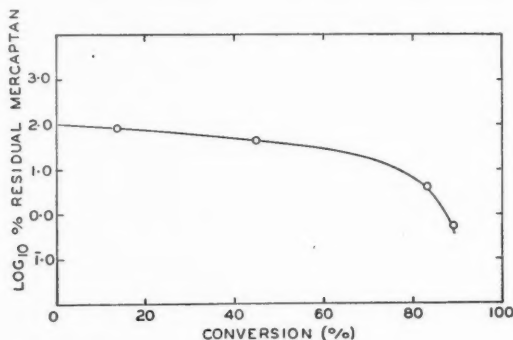


FIG. 1. Evaluation of the regulating index of polystyrene.

reaction vessel was reduced from a 4-oz. to a 1-oz. bottle. This permitted a more accurate estimate of the residual mercaptan. With the 1-oz. bottle no sampling was involved, the residual mercaptan being determined on the entire charge by amperometric titration with silver nitrate. The per cent conversion was obtained on a duplicate bottle by precipitating the latex in 300 cc. of butanol with vigorous agitation. This was followed by washing with water, drying in a vacuum overnight, and weighing.

Results and Discussion

RELATION BETWEEN $[\eta]$ AND \bar{M}_v FOR POLYSTYRENE PREPARED IN EMULSION AND THAT POSSESSING THE KUHN-SCHULZ CHAIN LENGTH DISTRIBUTION

With the aid of Equation (17) and the measured values of f and r , it was possible to estimate the viscosity heterogeneity index h_v of all the polymers prepared in emulsion, assuming a value of 0.78 for a . The values of h_v calculated in this manner are shown in Table I.

TABLE I
CALCULATED VISCOSITY HETEROGENEITY INDEX

Polymer No.	1	2	3	4	5	6	7	8	9	10	11
$f\%$	44.9	46.7	42.7	45.7	50.2	56.6	56.0	56.6	53.3	56.8	50.7
h_v	2.02	2.02	2.01	2.02	2.04	2.09	2.09	2.06	2.06	2.09	2.05
$\bar{M}_n \times 10^{-3}$	199	208	196	92	103	111	50.9	47.0	25.3	25.7	25.1
$[\eta]$	1.390	1.450	1.448	0.850	0.890	0.900	0.495	0.480	0.345	0.300	0.340
$r = 2.02, a = 0.78$											

The values of h_v for these polymers were essentially constant and did not differ significantly from the value $h_v = 1.90$ which corresponds to the Kuhn-Schulz distribution of chain length.

In Fig. 2, Curve 1, the logarithm of the intrinsic viscosity of each of the unfractionated polymers Nos. 1-11 is plotted against the logarithm of the number average molecular weight determined by the disappearance of mercaptan. The relation is seen to be linear and corresponds to the equation

$$[\eta] = 11.5 \times 10^{-5} M_n^{0.77}.$$

This type of relation is not peculiar to polystyrene prepared in the presence of tertiary dodecyl mercaptan. Ewart, Tigney, and Wales (1, 4) who prepared polystyrene by oil phase polymerization at 60°C., using carbon tetrachloride as modifier (2), obtained a similar result shown graphically by Curve 2, Fig. 2. The relation between the intrinsic viscosity of this unfractionated polystyrene determined in benzene and the number average molecular weight measured osmotically was found to be

$$[\eta] = 7.54 \times 10^{-5} M_n^{0.783}$$

over the range in molecular weight from 50,000 to 800,000. This result compares favorably with the relation found above between the intrinsic viscosity

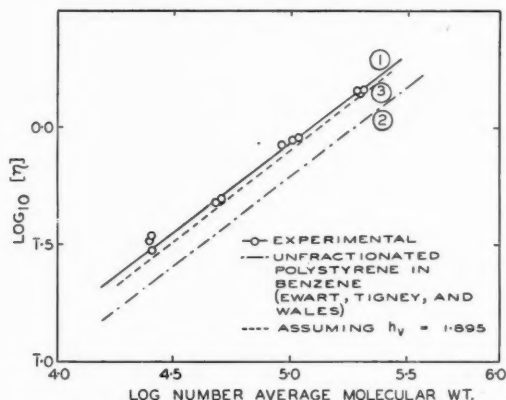


FIG. 2. Relation between the intrinsic viscosity and the number average molecular weight.

measured in toluene and the number average molecular weight determined by mercaptan disappearance over the molecular weight range 25,000 to 200,000.

The value of K in Mark's equation

$$[\eta] = K(M_v)^a = K(M_n h_v)^a$$

may be determined since $[\eta]$, M_n , a , and h_v are known for each of the polystyrenes Nos. 1-11. Assuming a value of 0.78 for a the average value of K over the molecular weight range investigated is 6.30×10^{-5} . If the values of K and a are assumed to remain constant over this molecular weight range, it is possible to determine $[\eta]$ corresponding to a given number average molecular weight and h_v . Such a relation is represented by Curve 3, Fig. 2, where h_v is taken as 1.90, the value for the Kuhn-Schulz distribution, and a is taken as 0.78.

If the scission of polystyrene possessing the Kuhn-Schulz distribution of chain length is random, the relation between the intrinsic viscosity and the number average molecular weight will be given by Curve 3, Fig. 2. Since the polystyrene prepared in emulsion possessed a slightly different chain length distribution, the relation between the number average molecular weight and the intrinsic viscosity should gradually shift from Curve 1 to Curve 3 in Fig. 2, during the course of the degradation. Since the distance between these two lines is not greatly in excess of the experimental error, the use of Curve 1 to obtain the relation between $[\eta]$ and M_n during degradation of polystyrene with a number average molecular weight in the range 25,000 to 200,000 was considered justified.

THE DEGRADATION OF POLYSTYRENE POSSESSING THE KUHN-SCHULZ DISTRIBUTION OF CHAIN LENGTH

The extent of polystyrene chain scission appeared to depend upon temperature, time, mass of oxidizing agents, and length of time of exposure to light.

Below 144°C. the extent of thermal scission was negligible as shown by the following experiment. A 16% toluene solution of polystyrene (16 gm. polystyrene per 100 cc. of toluene) was prepared using polystyrene No. 5. This was introduced into 5 cc. vessels, which were then reweighed to determine the polymer content. These vessels were flushed with nitrogen to displace the atmospheric oxygen and sealed off. After one week in a thermostat in the absence of light the vessels were removed and the intrinsic viscosities remeasured. No observable decrease in viscosity was detected at either 100°C. or 144°C.

As the extent of thermal scission at 100°C. was negligible, the scission by the action of benzoyl peroxide at this temperature could be investigated in the absence of simultaneous thermal degradation. Seven samples of benzoyl peroxide, ranging in weight from 0.001 to 0.1 gm., were weighed into seven 5 cc. glass vessels. A 2 cc. charge of a 16% solution of polystyrene No. 5 (\bar{M}_n 103,000) was added to each and the total weight redetermined. As in the former experiment, the vessels were flushed with nitrogen and sealed off. After heating the reaction vessels for 24 hr. at 100°C. they were reopened and the intrinsic viscosity of the contents measured. This procedure was repeated, employing polystyrene No. 6 (\bar{M}_n 111,000) at a temperature of 80°C. The logarithm of the number average molecular weight after degradation was obtained from the measured values of the intrinsic viscosity with the aid of Curve 1, Fig. 2. The average number of scission points per structural unit \bar{s} was then determined from the number average molecular weight by means of Equation (3). The results are shown in Fig. 3 where \bar{s} is plotted as a function of the number of moles of benzoyl peroxide per mole of styrene.

If the scission of polystyrene by benzoyl peroxide were not only random but proportional to the mass of benzoyl peroxide added, a linear relation should

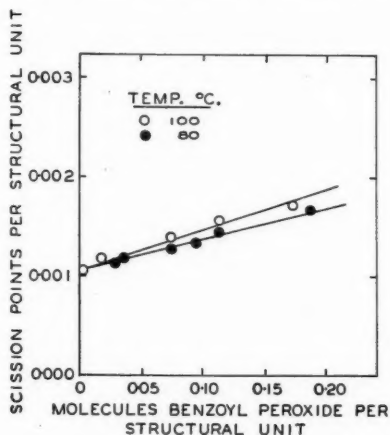


FIG. 3. The degradation of polystyrene in toluene solution by benzoyl peroxide and air.

exist between the mass of benzoyl peroxide added to the polystyrene solution and \bar{s} determined by viscosity measurements. Fig. 3 shows that such a linear dependence was found to exist over the range investigated both at 100°C. and 80°C.

The apparent success of the method of estimating the average number of scission points per structural unit by viscosimetric measurements suggests a method of following the kinetics of the scission of polystyrene by scission agents in solution, and also of estimating the relative effectiveness of a given mass of catalyst in causing the cleavage of polystyrene.

This work also suggested that one of the reasons for the apparent convergence of the viscosities of toluene solutions containing the same total weight concentration but various proportions of styrene and polystyrene, described by Mesrobian and Tobolsky (17), lay in the nature of the dependence of the intrinsic and concentrated solution viscosity upon the number average molecular weight. After the polymer has undergone a considerable amount of degradation the number of linkages that must be severed to yield a measurable change in viscosity is very large.

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THE DEGRADATION OF POLYSTYRENE

III. THE SCISSION OF POLYSTYRENE BY A VARIETY OF AGENTS AND THE ROLE PLAYED BY THE SOLVENT IN THIS PROCESS¹

BY D. S. MONTGOMERY² AND C. A. WINKLER

Abstract

For a number of polystyrenes possessing the Kuhn-Schulz chain length distribution but of different mean chain length, the relation was established between the intrinsic viscosity and the corresponding relative viscosity of a 16% solution in toluene, to facilitate the study of the scission process under conditions similar to those employed by Mesrobian and Tobolsky. It was found that this relation failed to distinguish between those scission points introduced during polymerization and those due to the subsequent degrading action of benzoyl peroxide and air. Assuming polystyrene prepared in a similar manner to that described by Mesrobian and Tobolsky possessed the Kuhn-Schulz chain length distribution it was possible to show that the average number of scission points per structural unit was a linear function of the mass of benzoyl peroxide added to the system and the number of hours exposure to light. The thermal degradation of polystyrene was studied both in the presence and the absence of toluene, and the role of the solvent in the scission of polystyrene by benzoyl peroxide and air was investigated.

Introduction

In their preliminary experiments on the simultaneous degradation of polystyrene and polymerization of styrene Mesrobian and Tobolsky (8) employed solutions containing 16 gm. polystyrene per 100 cc. of toluene. To facilitate the study of the scission reaction at this concentration it was desirable to establish the relation between the changes in the relative viscosity of the concentrated solution and the corresponding changes in the number average molecular weight of polystyrene possessing the Kuhn-Schulz distribution of chain length. The dependence of the intrinsic viscosity upon \bar{M}_n for polystyrene of this functional form of chain length distribution has already been established (9). Consequently, it was only necessary to derive a relation between the intrinsic viscosity of the polymer and the relative viscosity of the concentrated solution.

Fox and Flory (5) showed that the logarithm of the melt viscosities of fractionated samples of polystyrene and polyisobutylene with molecular weights ranging from 5000 to 100,000 was a linear function of the square root of the molecular weight, that is,

$$\log \eta = A + C\bar{\eta}_w^{1/2}, \quad (1)$$

where η is the melt viscosity, $\bar{\eta}_w$ is the weight average molecular weight and A and C are constants. Flory (3, 4) has shown this relation to be valid for polyesters of random chain length, as well as for all mixtures of molecules of

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a given polyester series. In the present experiments toluene may be regarded as fulfilling the role of a low molecular weight polystyrene of chain length y_1 . The weight average chain length for the solution \bar{y}_{ws} is then given by

$$\begin{aligned}\bar{y}_{ws} &= W_1 y_1 + W_2 \Sigma W_x y_x \\ \bar{y}_{ws} &= y_1 + W_2 (\bar{y}_{w2} - y_1),\end{aligned}$$

where W_1 and W_2 are the weight fractions of the solvent and polymer respectively, $\Sigma W_x y_x$ represents the sum of the products of the weight fractions and chain lengths of the polymer molecules, and \bar{y}_{w2} is the weight average chain length of the polymer. If η and η_1 represent the viscosities of the solution and solvent respectively, then η_r , the relative viscosity, is given by the quotient $\frac{\eta}{\eta_1}$.

Since from Equation (1)

$$\begin{aligned}\log \eta &= A + C(\bar{y}_{ws})^{1/2} \\ \text{and } \log \eta_1 &= A + C(y_1)^{1/2},\end{aligned}$$

$$\text{therefore } \log \eta_r = Cy_1^{1/2} \left[\left(1 + W_2 \frac{(\bar{y}_{w2} - y_1)}{y_1} \right)^{1/2} - 1 \right]. \quad (2)$$

Equation (2) is assumed valid for all concentrations of polymer, i.e., for $0 \leq W_2 \leq 1$. Since for a high polymer $\bar{y}_{w2} \gg y_1$, then

$$\frac{\bar{y}_{w2}}{y_1} - 1 \doteq \frac{\bar{y}_{w2}}{y_1}.$$

If the magnitude of W_2 is restricted so that the following relation is satisfied

$$\left(1 + W_2 \frac{y_{w2}}{y_1} \right)^{1/2} \doteq \left(\frac{W_2 \bar{y}_{w2}}{y_1} \right)^{1/2} \gg 1,$$

$$\text{then } \log \eta_r \doteq Cy_1^{1/2} \left(\frac{W_2 \bar{y}_{w2}}{y_1} \right)^{1/2}. \quad (3)$$

Flory has established that

$$[\eta] = \left(\frac{\log_e \eta_r}{W_2} \right) \doteq \frac{C}{2y_1^{1/2}} \bar{y}_{w2}. \quad (4)$$

$W_2 \rightarrow 0$

By taking the logarithm of both sides of Equations (3) and (4) and eliminating $\log \bar{y}_{w2}$, the following expression is obtained

$$\log \log \eta_r = \log C + 1/2 \log W_2 - 1/2 \log \frac{C}{2y_1^{1/2}} + 1/2 \log [\eta], \quad (5)$$

indicating a linear relation between $\log \log \eta_r$ and $\log [\eta]$ with a slope of 0.5 at constant weight fraction W_2 of polymer in the concentrated solution.

In the present paper, experiments were made to ascertain whether this relation would be valid for monomer-free polystyrene prepared in emulsion, and further to determine whether it would remain valid after the polymer had undergone degradation with benzoyl peroxide and oxygen. This was necessary in view of the possibility that benzoyl peroxide might cause some chain branching, resulting in a higher relative viscosity of the concentrated

solution for a given value of the intrinsic viscosity after degradation. An attempt was also made to investigate the action of air, benzoyl peroxide, and light upon the scission of polystyrene under conditions similar to those employed by Mesrobian and Tobolsky (8) but in the absence of styrene. In addition, the role played by the solvent in the thermal scission of polystyrene, as well as the scission of polystyrene by benzoyl peroxide and air in a variety of solvents, was studied.

Experimental Results and Discussion

Comparison of the Intrinsic Viscosity and the Relative Viscosity of 16% Solutions of Polystyrene in Toluene

Polystyrenes Nos. 2, 3, 5, 6, 7, and 9 described in the previous paper (9) were used. The characteristics of these polymers are listed in Table I.

TABLE I

Polymer No.	2	3	5	6	7	9
\bar{M}_n	208,000	196,000	103,000	111,000	50,900	25,300
$[\eta]$	1.450	1.448	0.890	0.900	0.495	0.345

Polystyrenes Nos. 2, 6, 7, and 9 were each dissolved in toluene to yield a concentration of 15.64 gm. polystyrene per 100 gm. of solution, similar to that employed by Mesrobian and Tobolsky (8). A 25.5 gm. quantity of each solution was introduced into a separate reversible viscosimeter. These differed in design from those employed by Mesrobian and Tobolsky only in that the bulb at the base of the capillary was enlarged to a capacity of 75 cc. After measuring the relative viscosity with respect to toluene at 25°C., a 2 cc. sample of the solution was withdrawn for the determination of the intrinsic viscosity of the dissolved polymer. Benzoyl peroxide was then added to the concentrated solution in the reversible viscosimeter in the ratio of 0.02 gm. per 10 gm. of polystyrene solution. The reversible viscosimeters were resealed, enclosing approximately 60 cc. of air, and placed in an oil bath at 100°C. for 16 hr. At the conclusion of this period the viscosimeters were withdrawn, the relative viscosity at 25°C. was measured, and a sample of the solution was again withdrawn for the determination of the intrinsic viscosity. This cycle of operations was repeated for the various polymers and the data thus obtained are represented in Fig. 1. The points are all seen to lie on a common straight line, indicating that this relation fails to distinguish between those scission points which had been introduced by the transfer agent during the formation of the polymer and those due to the subsequent degrading action of benzoyl peroxide and air. Consequently, the relation between the intrinsic viscosity and the relative viscosity of the concentrated solution during the degradation of polystyrene failed to give any indication of chain branching. However, the experimental results do appear to be in accord with the relation deduced in the Introduction which requires $\log_{10} \log_{10} \eta_r$ and $\log_{10} [\eta]$ to be linear functions of the logarithm of the weight average molecular weight.

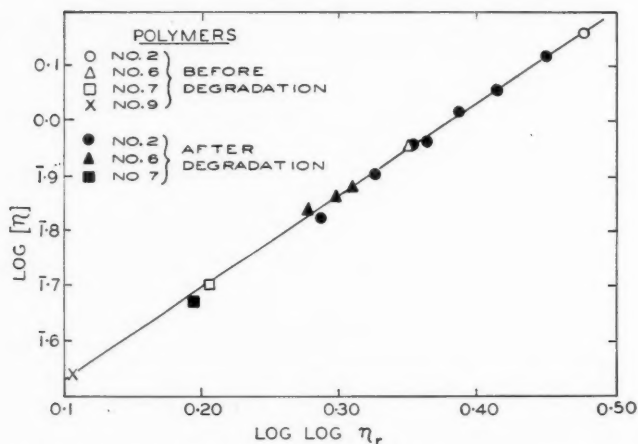


FIG. 1. The relation between the intrinsic viscosity and the concentrated solution viscosity of unfractionated polystyrene prepared in emulsion before and after degradation by benzoyl peroxide and air.

Anomalous behavior was observed upon the degradation of the polystyrene of lowest molecular weight by benzoyl peroxide and air. A slight increase in the relative viscosity of the concentrated solution was observed after the first increment of benzoyl peroxide. Thereafter the relative viscosity decreased in the regular manner. This observation had previously been observed in a qualitative experiment in which a trace of monomer was present with the polymer. It seems doubtful that even traces of monomer could exist after the washing and drying treatment given the polymers prepared in emulsion, and the significance of this result is therefore not clear.

The relation between the average number of scission points per structural unit and the number of molecules of benzoyl peroxide per structural unit, during the degradation of Polystyrene No. 2 in the previous experiment, is shown in Fig. 2. The relation between these quantities during the degradation of the same polymer by benzoyl peroxide in the absence of air, described in the previous paper (9, Fig. 3), is also shown in this figure. Apparently, the small change in the air-benzoyl peroxide ratio in the viscosimeters, due to the withdrawal of 2 cc. of polymer solution for the determination of the intrinsic viscosity, was insufficient to cause any observable curvature, as was the change in air-benzoyl peroxide ratio caused by making the final addition of benzoyl peroxide three times as large as the preceding one. However, it may be seen that the slope of the line when air was present to that when it was excluded is 4.5/1. The extent of scission per mole of benzoyl peroxide was evidently considerably enhanced by the presence of air.

Ewart (2) found that the relation between $[\eta]$ and \bar{M}_n for unfractionated polystyrene prepared in the presence of benzoyl peroxide at 60°C. was iden-

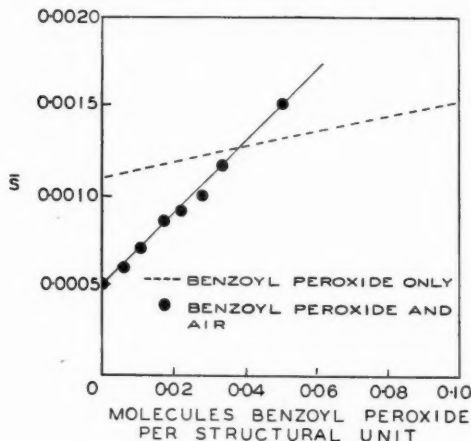


FIG. 2. The degradation of Polystyrene No. 2 by benzoyl peroxide in the presence and absence of air at 100°C.

tical with that for unfractionated polystyrene prepared in the presence of carbon tetrachloride. This suggested that the functional form of the chain length distribution of these polymers did not differ widely from the Kuhn-Schulz relation. If this assumption is correct, it is reasonable to assume further that the polystyrene prepared by Mesrobian and Tobolsky (8) by bulk phase polymerization in the presence of benzoyl peroxide at 100°C. also possessed this form. This would allow the course of degradation in solution to be followed by employing the relations established between $\log_{10} \log_{10} \eta_r$ and $\log_{10} [\eta]$, and between $\log_{10} [\eta]$ and \bar{M}_n to determine the average number of scission points as a function of the added mass of benzoyl peroxide and air or the number of hours of exposure to light radiation.

A polystyrene was therefore prepared under conditions similar to those employed by Mesrobian and Tobolsky (8) in the preparation of their three-hour sample. Benzoyl peroxide (0.1772 gm.) and styrene (177.2 gm.) were introduced into a 220 cc. glass vessel. The styrene had previously been washed with *N*/10 sodium hydroxide, dried over calcium chloride, and distilled under reduced pressure. The vessel was sealed off in air and heated for three hours at 100°C. After the vessel had been opened, the contents was thoroughly washed with methanol and dried overnight in a vacuum oven at 76°C. The yield of polymer thus obtained was 40.7%.

Ten cubic centimeters of a solution containing 16 gm. of this polymer per 100 cc. of toluene was placed in a reversible viscosimeter, which was sealed off in air. After the concentrated solution viscosity had been measured, the viscosimeter was opened and charged with 0.005 gm. of benzoyl peroxide, as well as a fixed amount of air. The temperature of the viscosimeter was then maintained at 100°C. for 16 hr. before the viscosity was again measured and the

system recharged with these scission agents. Fig. 3 shows the linear relation found between the number of scission points determined from the measurement of the relative viscosity and the mass of benzoyl peroxide added to the system.

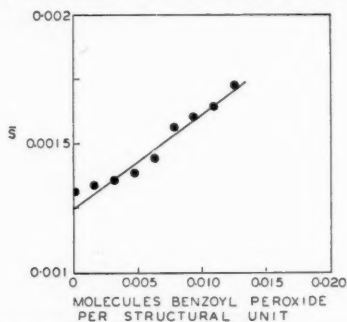


FIG. 3. The degradation of polystyrene in toluene solution by benzoyl peroxide and air. Concentration, 16 gm. polystyrene per 100 cc. toluene. Temperature, 100°C.

The same polymer solution was introduced into a second reversible viscosimeter with a fixed quantity of air and sealed. The reversible viscosimeter was then suspended 5 cm. above a G.E. Type RS Sunlamp (275 watts λ 3200 – 7000 Å) in an air oven maintained at 100°C. This viscosimeter was periodically removed for the determination of the relative viscosity at 25°C. to estimate the extent of scission. In Fig. 4 the results of this experiment are shown. Following a marked initial curvature due to the air initially sealed into the viscosimeter, a linear relation was found to exist between the length of exposure of the polymer solution to light and the number of scission points determined from the viscosity measurements.

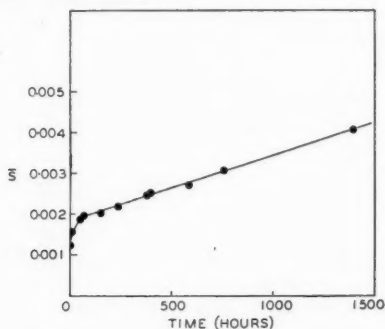


FIG. 4. The degradation of polystyrene in toluene solution by light and air. Concentration, 16 gm. polystyrene per 100 cc. toluene. Temperature, 100°C.

The Thermal Degradation of Polystyrene Prepared in Emulsion

To gain an insight into the role played by the solvent in the thermal degradation of polystyrene, experiments were made in which polystyrene was thermally degraded, both in the presence and the absence of solvent. It was hoped

that these data would yield information on the influence of the toluene upon the activation energy and frequency factor of the scission process. Preliminary experiments indicated that the decomposition of the solid polymer prepared in emulsion was affected by the quantity of mercaptan introduced into the polymer during its preparation. Thus, when the sealed reaction tubes containing solid Polystyrene No. 5 (\bar{M}_n 103,000) were opened after thermal degradation in the absence of air at 247°C. and 259.7°C., a strong smell of hydrogen sulphide was detected. A copper wire immersed in a toluene solution of this polymer after thermal degradation rapidly turned black. On the other hand, the higher molecular weight Polystyrene No. 3 (\bar{M}_n 196,000) did not yield a detectable quantity of hydrogen sulphide after thermal degradation, nor did Polystyrene No. 5 when thermally degraded in toluene solution. This anomalous liberation of hydrogen sulphide obscured the interpretation of the influence of toluene upon the activation energy and frequency factor of thermal scission. The experimental details concerning this study on the degradation of polystyrene are as follows. Samples of 0.2 gm. of each polystyrene were weighed into Pyrex tubes sealed at one end. These tubes were flushed three times with nitrogen and sealed off under vacuum. They were placed in a thermostat, withdrawn after measured intervals of time, and the intrinsic viscosity of the contents was determined.

The thermal degradation of polystyrene in toluene solution was studied by introducing 1.5 cc. of a 16% solution of Polystyrene No. 5 in toluene into seven weighed heavy walled Pyrex tubes of 0.5 cm. bore. After filling, the tubes were reweighed to determine the weight of the solution, and sealed onto the evacuation apparatus. The lower portion of the tubes containing the solution were cooled in dry ice - acetone mixture, while the space above the solution was flushed three times with nitrogen. The tubes were then evacuated, sealed off, and placed in a thermostat. They were withdrawn after measured intervals of time and the intrinsic viscosity of the polymer determined.

By assuming that the thermal scission was random, the average number of scission points per structural unit was estimated from the measured values of the intrinsic viscosity as previously outlined. The results thus obtained are shown in Figs. 5 and 6.

From Fig. 6 it can be seen that at each temperature the relation between \bar{s} and the time of degradation is linear for Polystyrene No. 3. This implies that the scission was essentially random and that the rate of scission at each temperature was constant. However, on the thermal degradation of Polystyrenes Nos. 5 and 6 prepared in emulsion, the plot of \bar{s} against time at 247°C. and 259.7°C. shows marked curvature. This anomaly was associated with the liberation of hydrogen sulphide from the polymer, previously discussed.

Unfortunately, the results of the degradation of Polystyrene No. 5 in solution were erratic and did not permit the estimation of the activation energy of the scission process. However, the data represented in Fig. 5 indicate that the rates of scission appeared to be considerably less than the corresponding rates in the absence of solvent.

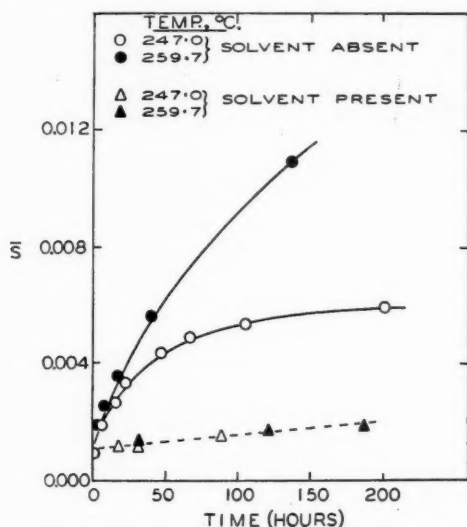


FIG. 5. The thermal degradation of emulsion polymerized Polystyrene No. 5 (\bar{M}_n 103,000), both in the presence and the absence of toluene and the thermal degradation of Polystyrene No. 6 at 247°C.

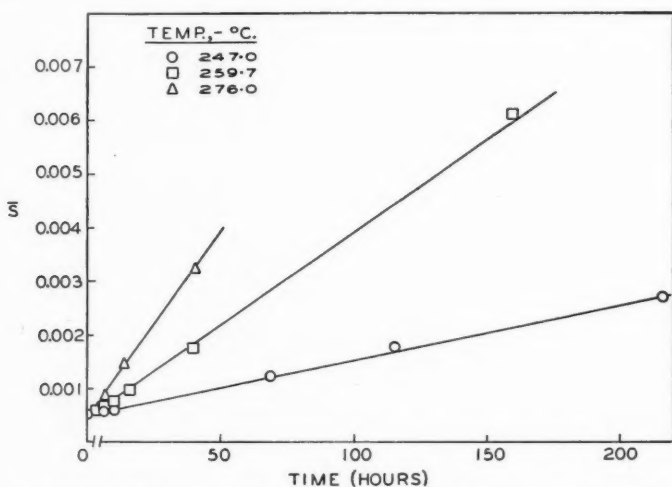


FIG. 6. The thermal degradation of emulsion polymerized Polystyrene No. 3 (\bar{M}_n 196,000) at various temperatures in the absence of solvent.

To determine the influence of modifier molecules present in the polymer on the rate of thermal scission, some pure polystyrene was degraded under the same conditions. The polystyrene for this experiment was prepared by introducing 60 cc. of distilled styrene into a fire polished glass vessel which was subsequently sealed into the evacuation and filling apparatus. The styrene

was boiled under reduced pressure, and the space above the monomer was swept three times with nitrogen. Finally the tube was surrounded with a dry ice - acetone mixture and the space above the styrene thoroughly evacuated. The tube was sealed off and placed in a thermostat at 100°C. for 22 hr. The contents was washed with several 100 cc. portions of methanol to remove the monomer and dried overnight in a vacuum oven at 76°C.

The degradation of this material in the absence of solvent was studied in the manner previously described. The results are shown in Fig. 7. It may be seen that at each temperature a linear relation exists between \bar{s} and the time of degradation. This indicates that the functional form of the distribution in this polymer is not widely different from that of the polymer prepared in emulsion. This is in accord with the results of Schulz and Dinglinger (10, 11, 12) who showed that at 60% conversion polystyrene prepared by bulk phase polymerization at 140°C., in the absence of catalyst, possessed essentially the Kuhn-Schulz chain length distribution.

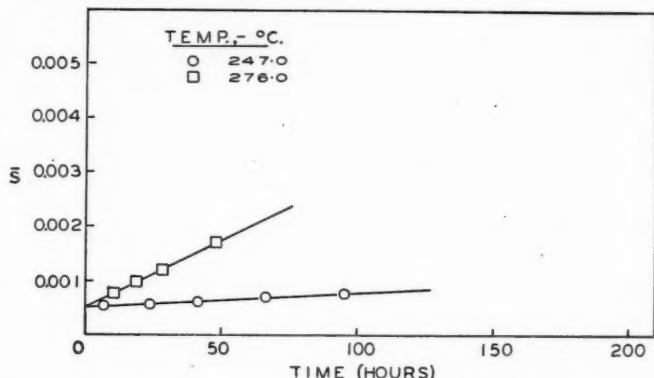


FIG. 7. The thermal degradation in the absence of solvent of polystyrene prepared under conditions where air and catalyst were excluded.

From the limited data on the rates of scission determined at various temperatures the activation energy of the scission process for Polystyrene No. 3 (\bar{M}_n 196,000) prepared in emulsion was estimated to be of the order of 40 kcal. per mole, and for the depolymerization of the pure polystyrene prepared in bulk phase of the order of 42 kcal. per mole. This value is intermediate between the value of 34 kcal. per mole reported by Votinov (13) and the value of 44 kcal. per mole reported by Jellinek (6).

The Degradation of Polystyrene by Benzoyl Peroxide in Various Solvents

The primary step in the degradation of polystyrene in solution by benzoyl peroxide and oxygen was visualized as involving the decomposition of these scission agents into free radicals. Some of these free radicals were assumed to undergo collision with the polymer molecules while others were considered to attack the solvent first, transferring the active center to the solvent molecules.

If the assumption is made that any solvent molecules thus affected are capable of causing the scission of polymer chains, the solvent would clearly be involved in the scission process, and the extent of scission resulting from a given mass of benzoyl peroxide should depend on the capacity of the solvent to act as a transfer agent.

To study the degradation of polystyrene in various solvents, 2% solutions (i.e., 2 gm. polystyrene per 100 cc. of solvent) were used. By reducing the concentration of the polymer to this value the probability of direct attack of the free radicals derived from benzoyl peroxide upon the polymer was minimized; this permitted the role of this solvent to be more clearly discerned.

The polystyrene used in this experiment was prepared by bulk phase polymerization of styrene in the presence of air and benzoyl peroxide at 100°C., the procedure described on page 433 being followed precisely. It was assumed that the chain length distribution of this polymer was given by the Kuhn-Schulz relation.

The solutions were prepared by dissolving 1.2 gm. of this polystyrene in 60 cc. of each of the following solvents: methyl ethyl ketone, toluene, ethyl acetate, and carbon tetrachloride. The solutions were filtered and three viscosimeters were charged with 10 cc. of each solution. The 12 viscosimeters were sealed in air and immersed in an oil thermostat at 80°C. A limited amount of polystyrene degradation occurred over a four-day period at this temperature owing to the included air. After the viscosity had been remeasured the viscosimeters were opened and charged with 0.005 gm. benzoyl peroxide and a fixed quantity of air. The viscosimeters were then resealed and returned to the thermostat for 16 hr. prior to the measuring of the viscosity and the recharging.

To relate the changes in viscosity to the corresponding changes in number average molecular weight, it was assumed that both the polystyrene prepared in the presence of benzoyl peroxide and in emulsion possessed the Kuhn-Schulz chain length distribution. Two per cent solutions were made using Polystyrenes 3, 4, 5, 7, and 9, prepared in emulsion, and each of the above solvents. By measuring the viscosities of these solutions the relations were established between the viscosities of these 2% solutions and the number average molecular weight of the dissolved polymer in each of the solvents mentioned. This relation is shown in Fig. 8, where $\log_{10} \log_{10} \eta_r$ is plotted against the logarithm of the number average molecular weight. By using this graph the average number of scission points per structural unit could be determined from the relative viscosities of the 2% solutions of the polymers prepared in bulk phase. The results for the degradation studies in the various solvents are shown in Fig. 8. On the assumption that the scission is due entirely to benzoyl peroxide, the slopes of these lines represent the average number of scission points obtained per molecule of benzoyl peroxide. Actually the oxygen in the included air was responsible for a fraction of the total amount of scission, and, if the

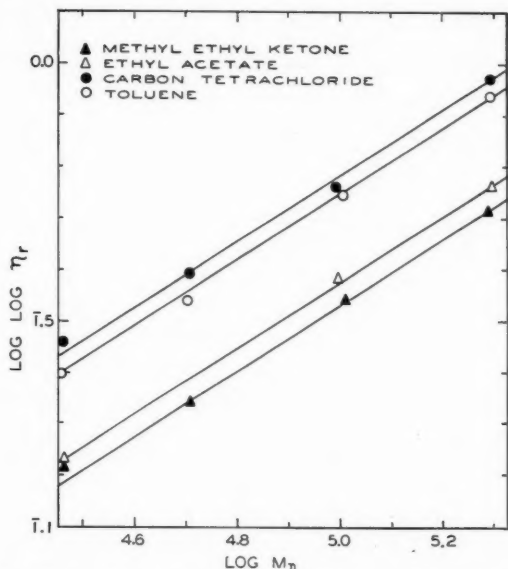


FIG. 8. Relation between the viscosity of 2% solutions of polystyrene possessing the Kuhn-Schulz chain length distribution in various solvents and the molecular weight.

ratio of the mass of benzoyl peroxide to air is altered, the apparent number of scission points resulting from a given mass of benzoyl peroxide will be changed. In this experiment the air space in the viscosimeter above the solution was approximately 20 cc. However, it was difficult to estimate quantitatively the amount of oxygen that diffused into the viscosimeter on the recharging with benzoyl peroxide. By keeping constant the time during which the viscosimeters were open, and by maintaining the time of degradation at 16 hr., the total quantity of oxygen admitted and the fraction of oxygen consumed were assumed to remain fixed for each solvent.

The average number of scission points per molecule of benzoyl peroxide was estimated from the slopes of the lines in Fig. 9 in the region corresponding to the first five equal increments of benzoyl peroxide. The values thus obtained were 0.003, 0.001, 0.03, and 0.45 scission points per molecule of benzoyl peroxide for methyl ethyl ketone, toluene, ethyl acetate, and carbon tetrachloride respectively. The extent of chain scission in carbon tetrachloride was so high that the experiment was discontinued after the second addition of benzoyl peroxide, at which point the number average molecular weight of the polymer was 9440, a value considerably lower than that of any of the polymers prepared in emulsion. This high efficiency of chain scission in carbon tetrachloride (approximately one scission point for every two molecules of benzoyl peroxide) is in accord with other observations (1, 7) on the efficiency of carbon tetrachloride as a chain transfer agent.

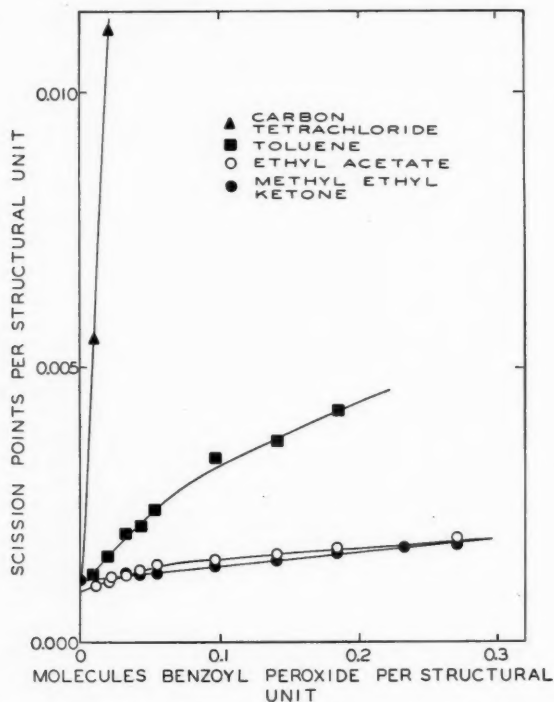


FIG. 9. The degradation of polystyrene by benzoyl peroxide and air in various solvents at 100°C.

After the first five additions of benzoyl peroxide the size of the increments was increased from 0.005 gm. to 0.02 gm. This changed the ratio of air to benzoyl peroxide, causing an apparent decrease in the number of scission points per molecule of benzoyl peroxide. This effect, which was less marked in methyl ethyl ketone than in toluene and ethyl acetate, indicates that the influence of the enclosed air is by no means negligible.

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NOTES

The Oxidation of Cholesteryl Acetate Dibromide

The degradative oxidation of cholesteryl acetate dibromide with chromic acid (1, 2, 3, 4) was studied with a view to discovering the effects of temperature, acid concentration, and reaction time on the rates of formation of the acid and ketonic fractions, and on the rate of chromic acid consumption. The ketonic fraction included only those hydroxyketones that yielded ether-insoluble acetate semicarbazones.

In a typical experiment, cholesteryl acetate dibromide (15 gm.) was dissolved in 750 ml. glacial acetic acid in a 2 liter three-necked flask, fitted with stirrer and condenser. The flask was immersed in a constant-temperature bath maintained at 50°C. A solution of 30 gm. chromium trioxide, 30 ml. water, and 5.6 ml. concentrated sulphuric acid in glacial acetic acid (total volume 250 ml.) previously cooled to 2–5°C., was then added and the solution stirred vigorously.

At desired time intervals, 5 ml. samples were removed and titrated with standard sodium thiosulphate solution. At corresponding intervals, 100 ml. samples were removed, the excess chromic acid destroyed with methanol, and the solution concentrated at 40°C. to a small volume. The sample was diluted with water, extracted with ether, and the ether evaporated; the residue was debrominated with zinc in acetic acid, and, after dilution with water, extracted again with ether. The ether solution was extracted with 10% sodium hydroxide solution to obtain the acid fraction, isolated by acidifying the alkaline washes and filtering.

The residue obtained on evaporation of the ether solution was treated with semicarbazide hydrochloride and sodium acetate in ethanol; after four hours of refluxing, the alcoholic solution was diluted, extracted with ether, and the insoluble semicarbazones filtered.

It was observed that usually the ratio of acid to ketone fraction was roughly constant at 10:1, throughout the course of a given reaction, and with varying amounts of sulphuric acid present. At 60°C. with no sulphuric acid present, the yield of ketonic material is relatively higher, the ratio falling to 5:1.

Under all conditions, the yields of acid and ketonic fractions go through a maximum, indicating that all products are subject to attack by the oxidizing medium. The yield based on unrecovered cholesterol would be highest shortly after the start of the reaction, before the absolute maximum is reached, and when the consumption of cholesteryl acetate dibromide is still very small.

The effect of sulphuric acid is to decrease the time taken to reach the maximum yield; it serves to speed up the destruction of the desired products as

well as their formation. At 50°C., addition of sulphuric acid raises the yield at the maximum for both acid and ketones; thus, when 28.0 ml. of sulphuric acid per liter of reaction solution is present, the maximum is reached in five minutes instead of nine hours, and is 60% higher. At 60°C., however, addition of sulphuric acid decreases the maximum yield.

In any given reaction, there is no apparent correlation between chromic acid consumption and the yield of acid and ketonic fractions; with varying amounts of sulphuric acid, at 50°C., there was a fairly constant ratio of 250 moles of chromic acid consumed per mole of ketone (calculated as dehydroepiandrosterone) formed, at the maximum.

The highest yield of acid fraction was obtained at 50°C. with 16.8 ml. of sulphuric acid per liter of reaction solution, with reaction time of 30 min.; under these conditions, 5.10 gm. of crude acid was obtained from 15 gm. of cholesteryl acetate dibromide. This represents a yield of 48% calculated as 3- β -hydroxy- Δ^5 -cholenic acid acetate.

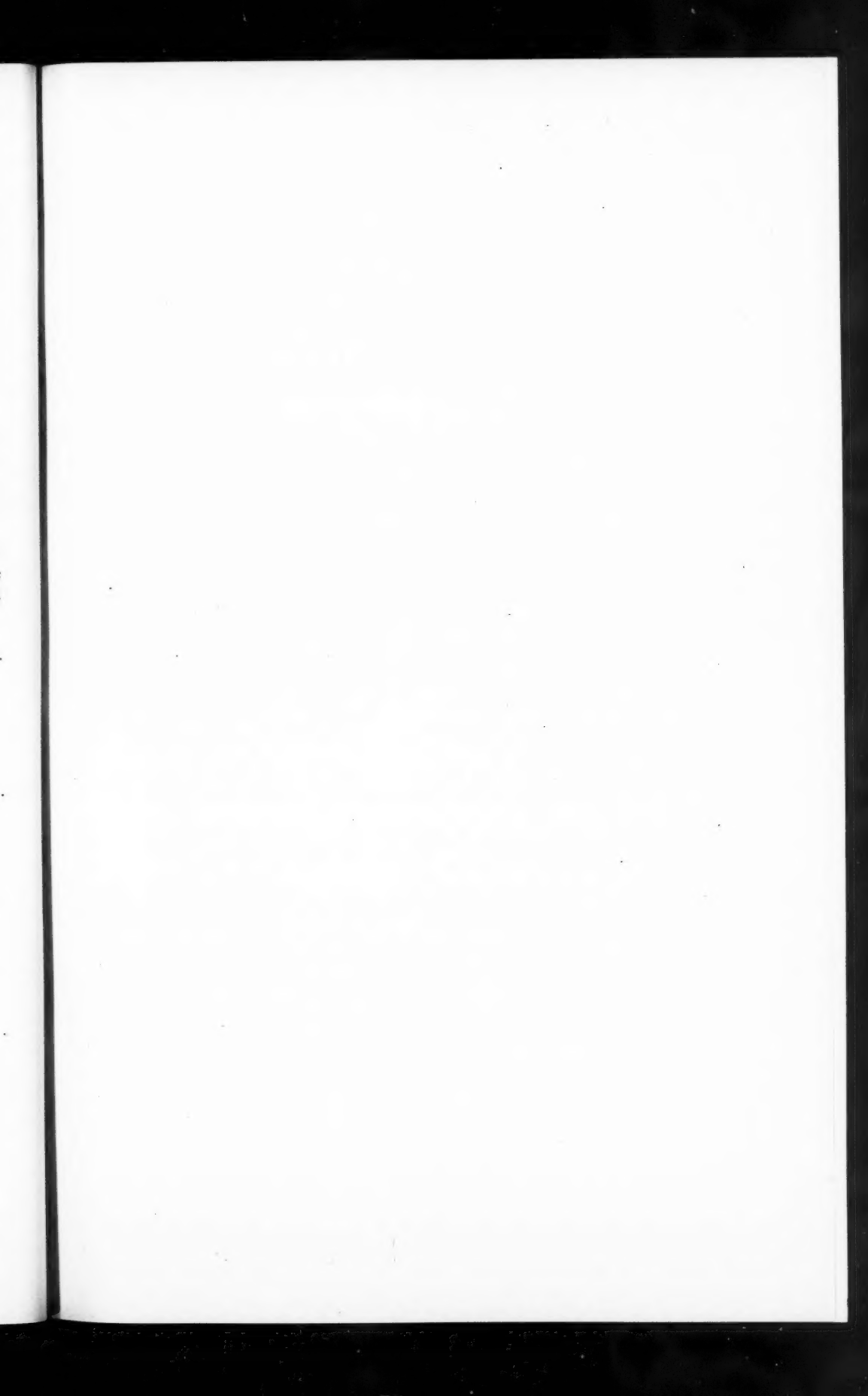
The highest yield of ketonic fraction was obtained at 60°C., with no sulphuric acid and a reaction time of 12 hr. These conditions yield 0.53 gm. of crude dehydroepiandrosterone acetate semicarbazone, corresponding to a crude yield of 5.3%.

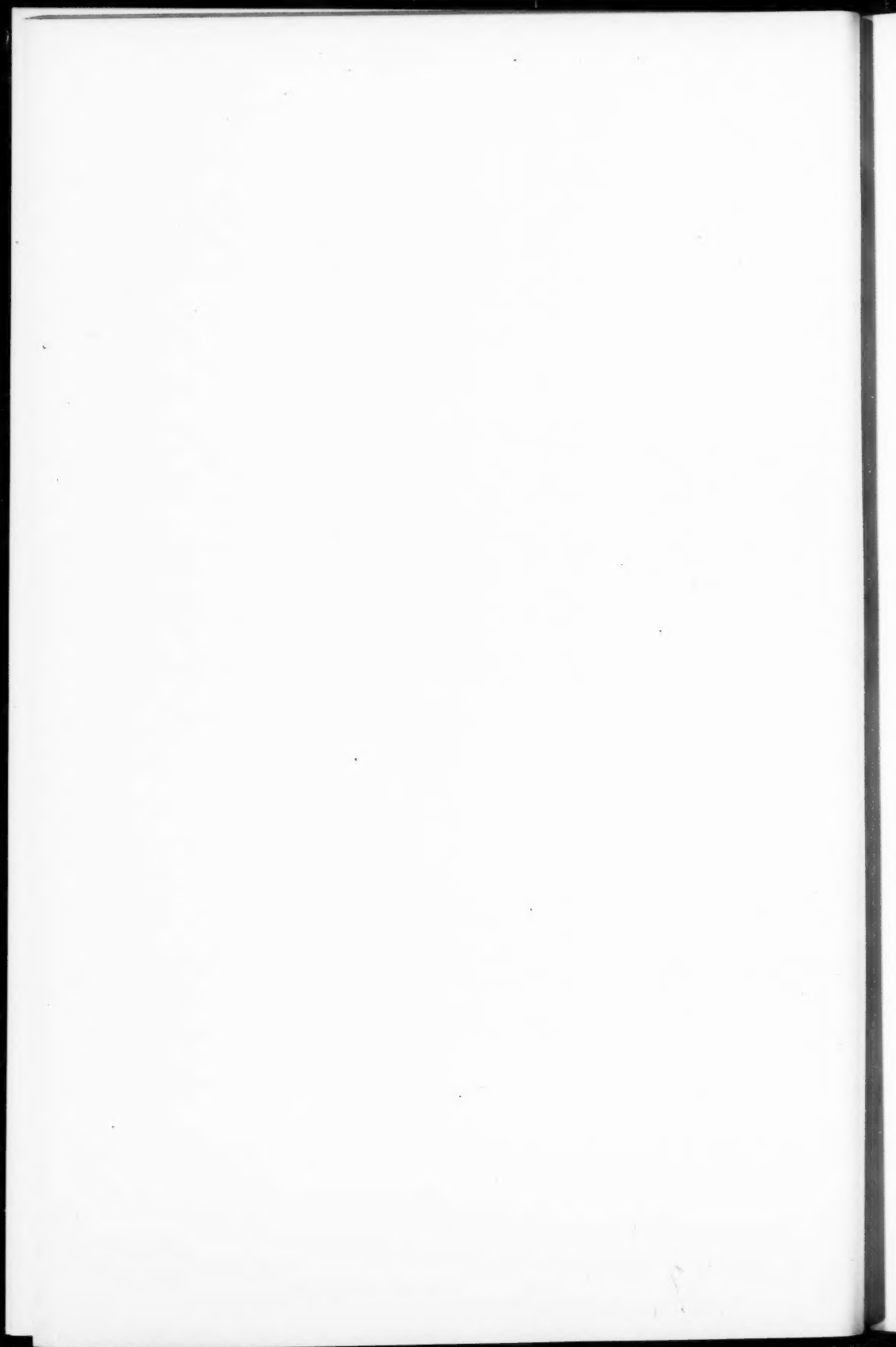
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ABSTRACT:—An abstract of not more than about 200 words, indicating the scope of the work and the principal findings, is required.

ILLUSTRATIONS:

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